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HYDRODENITROGENATION OF QUINOLINE AND ACRIDINE

BY

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BY

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ABSTRACT

The hydrodenitrogenation of quinoline and of acridine was studied in a batch autoclave reactor between 342 and 353°C and between 500 and 2000 psig. The several commercial hydrotreating catalysts examined decreased in activity in the following order for quinoline hydrodenitrogenation: Ni-Mo/Al_2O_3, Ni-W/Al_2O_3, Ni-W/SiO_2-Al_2O_3, and Co-Mo/Al_2O_3.

The total nitrogen removal rate for quinoline was slightly greater than that for acridine and both followed pseudo first-order kinetics over a conversion range of 0 to 50%. Hydrogenation and cracking steps were both kinetically limiting. Nitrogen-containing reaction products for quinoline hydrodenitrogenation were 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, decahydroquinoline and o-propylaniline. At 342°C and 500 psig quinoline and 1,2,3,4-tetrahydroquinoline were in thermodynamic equilibrium, and the disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline followed pseudo first-order kinetics. Sixteen nitrogen-containing reaction products were found for acridine hydrodenitrogenation,

including 1,2,3,4-tetrahydroacridine, 1,2,3,4,9,10, 13,14-octahydroacridine, sym-octahydroacridine, perhydroacridine, and o-(methylenecyclohexane)aniline. The hydrogenolysis step for both quinoline and acridine appears to be through hydrogenated forms of these compounds. This is supported by bond strength arguments.

CHAPTER I

INTRODUCTION

A. Scope of Research

A very promising technology for the production of clean fossil fuels is catalytic hydroprocessing of petroleum residua, coal-derived liquids and shale oil. Presently, there is limited understanding of the chemistry and engineering of existing processes for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum. It is also uncertain how to apply or to extend the petroleum technology to liquids derived from coal and shale oil.

One approach to understanding the catalytic chemistry of the complex processes of HDS and HDN is to study the reactivity of representative sulfur and nitrogen compounds found in various natural and processed petroleum stocks. This approach has been undertaken successfully in recent years by Cox and Berg (1962), Sonnemans (1973), Goudriaan (1974), Mayer (1974) and Cocchetto (1974).

The major objective of this research was to develop the techniques for studying HDN of multi-ring nitrogen-containing compounds under high-pressure liquid-phase conditions and to establish the HDN reaction network of acridine with a preliminary kinetic analysis. This work was conducted in a batch autoclave reactor system; quinoline was used in studies to develop HDN study techniques. The reactivity of acridine was then studied in the liquid phase with a highly hydroprocessed petroleum fraction, white oil, used as a carrier solvent. The white oil was a mixture of C_{18}-C_{36} naphthenic and paraffinic hydrocarbons and contained no sulfur, nitrogen or aromatic compounds. This was verified by our analysis schemes. The reaction network was studied from 300 to 400°C and a hydrogen pressure of 500 to 2000 psig over a sulfided Ni-Mo/Al_2O_3 catalyst (American Cyanimid HDS-9A). The aromatic nitrogen compound quinoline was used instead of acridine in preliminary experiments because its HDN reaction network is well documented (Goudriaan, 1974). These preliminary experiments include establishing experimental reactor procedures and reactor reproducibility and involved a nominal screening of various commercial hydroprocessing catalysts. These

catalysts include American Cyanimid HDS-16A (Co-Mo/Al_2O_3) and HDS-9A (Ni-Mo/Al_2O_3), Harshaw Ni4301 (Ni-W/Al_2O_3-SiO_2) and Ni4303 (Ni-W/Al_2O_3), and NALCO Nt-550 (Ni-W/Al_2O_3). All catalysts are studied in the sulfided state. A convenient analytical scheme for quantifying organic nitrogen compounds in white oil was developed utilizing a gas chromatograph with a nitrogen-specific detector. A gas chromatograph-mass spectrometer system was used to identify the reaction products of acridine.

B. Literature Survey

The purpose of this literature survey is to indicate that aromatic nitrogen-containing compounds such as quinoline and acridine are characteristically found in heavier petroleum fractions such as residua and coal-derived liquids, and such compounds are relevant to the study of the HDN process because of their limited reactivity. Excellent literature reviews concerning the broad areas of HDN and HDS have been compiled previously by Mayer (1974), Goudriaan (1974) and Schuit and Gates (1973).

All crude oils contain some nitrogen-containing compounds. Table I presents a summary of the

TABLE I

DISTRIBUTION OF NITROGEN IN U. S. PETROLEUM FIELDS [a]

Nitrogen Content, %	No. of Fields	Percentage of Fields
0.05	62*	40
0.05-0.10	35	23
0.10-0.20	29	19
0.20-0.50	22**	14
0.50	6***	4

* Texas and Wyoming fields primarily
** California and Wyoming fields
*** All California fields
a Tschamber and DeRuiter, 1966

nitrogen content in various United States petroleum fields. It appears that the California fields contain more nitrogen than other U.S. fields. Table II summarizes the nitrogen distribution in crude oils according to boiling point fractions. The nitrogen content increases with increasing boiling point fraction, and residuum contains about 50 wt% of the total nitrogen found in crude oil. Table III indicates that quinolines constitute 8 to 32 wt% of the total nitrogen content in crude oil distillates. Schultz et al. (1973) have reported that acridine is present in coal-carbonization products.

A crude classification of organic nitrogen compounds in oils is according to basicity. Basic compounds have pKa in water greater than 2; non-basic compounds have pKa in water less than 2. Table IV presents a list of nitrogen compounds classified according to basicity. Quinoline and acridine are basic compounds by this criterion. Table V presents a summary of the percentage of basic nitrogen compounds in crude oils. The ratio of basic nitrogen compounds to total nitrogen is nearly constant at 25 - 35%, regardless of the overall nitrogen content. This

TABLE II

DISTRIBUTION OF NITROGEN IN CRUDE OILS [a]

Crude Oil	1		2		3	
Boiling Range, °C	Wt.%	% of Total	Wt.%	% of Total	Wt.%	% of Total
Total	.23	100.0	.28	100.0	.16	100.0
275	.005	0.1	---	-----	.003	0.1
275-310	.026	0.4	.01	0.4	.024	0.6
310-338	.036	1.0	.02	0.4	.030	1.1
338-365	.058	1.4	.05	1.1	.059	1.9
365-393	.105	2.5	.09	1.8	.096	3.1
393-422	.144	4.0	.13	2.9	.136	6.3
Residuum	.50	91.3	.53	92.9	.44	87.5

a Tschamber and DeRuiter, 1966

TABLE III

NITROGEN COMPOUNDS IN CRUDE OIL DISTILLATES [a]

Group	Kuwait 152-327°C	California 370-455°C
Indoles	9.4	7.2**
Carbazoles	29.4	43.3***
Benzcarbazoles	----	5.6
Pyridines	44.0	8.9*
Quinolines	8.3	32.0*
Pyrroles	8.9	----
Phenanthridines	----	3.0
	100.0%	100.0%

* Contain in part both N and O heteroatoms
** About 50% n-alkyl substituted
*** About 20% n-alkyl substituted
a Tschamber and DeRuiter, 1966

TABLE IV*

NITROGEN COMPOUNDS CLASSIFIED ACCORDING TO BASICITY

Compound	pKa (H_2O)
Ammonia	9.27
Imidazol	7.03
2-Methylpyridine	6.5
Acridine	5.60
Pyridine	5.23
5,6-Benzquinoline	5.15
Isoquinoline	5.14
Dimethylaniline	5.10
6,7-Benzquinoline	5.05
Quinoline	4.94
N-methylaniline	4.78
3,4-Benzacridine	4.70
2,3-Benzacridine	4.52
1,10-Phenanthroline	4.27
7,8-Benzquinoline	4.25
2,2-Bipyridine	4.23
Quinazoline	3.51
Phthalazine	3.47
1,2-Benzacridine	3.45
Phenanthridine	3.30
4,7-Phenanthroline	3.12
1,7-Phenanthroline	3.11
Cinnoline	2.70
Pyrazole	2.53
Thiazole	2.53
Pyridazine	2.33
Benztriazole	1.6
Pyrimidine	1.30
Indazole	1.3
Phenazine	1.23
Diphenylamine	0.85
Quinoxaline	0.8
Pyrazine	0.6
Pyrrole	0.4
Indole	----
Propionitrile	-0.8
Carbazole	-1

* Richter et al. (1952)

TABLE V

PROPORTION OF BASIC NITROGEN COMPOUNDS IN CRUDE OILS [a]

Source	Basic N, Wt.%	Total N, Wt.%	N_B/N^*_T, %
Kuwait	.03	.12	25
TribuPetrolea	.033	.13	25
Mid Continent Mix	.025	.10	25
East Texas	.02	.08	25
West Texas	.03	.11	27
Wilmington	.14	.50	28
Santa Maria Valley	.19	.66	29
Ventura	.13	.42	31
Kansas	.04	.12	33
Kettleman Hills	.14	.41	34

*N_B designates basic nitrogen

N_T designates total nitrogen in all forms

a Tschamber and DeRuiter, 1966

implies that the types of compounds present do not vary with petroleum source.

Nitrogen is present in coal to a much greater extent than in petroleum as demonstrated in Table VI. Many nitrogen compounds can be isolated from distillation tars produced from coal. These compounds include pyrroles, pyridines, indoles, anilines, quinolines, carbazoles, and several other compound classes present in lesser amounts. It is well known that coal tar is a rich source of aromatic nitrogen compounds such that commercial separation of these is feasible. Thus, it is clear that the same types of nitrogen-containing compounds found in petroleum are likely to be present in coal-derived liquids. More importantly, information secured on the hydrodenitrogenation of the important classes of nitrogen compounds is useful in understanding nitrogen removal both from petroleum and from coal-derived liquids.

Catalytic hydroprocessing is part of the modern processing technology for removal of nitrogen from oils. Although the practice of catalytic hydrodenitrogenation (HDN) is important, the literature contains little practical information and almost no basic information about the catalytic chemistry.

TABLE VI

OCCURRENCE OF NITROGEN IN COAL [a]

	Nitrogen Wt.%
Peat	0.7-3.4
Brown Coal	0.4-2.5
Bituminous Coal	0.6-2.8
Anthracite Coal	0.2-1.5
Petroleum	0 -0.9

a Tschamber and DeRuiter, 1966

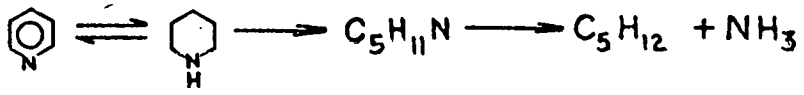
Removal of nitrogen is similar to removal of sulfur to the extent that processing severity increases strongly from light distillates to the heaviest feedstocks. Nitrogen removal should involve many of the same problems as sulfur removal especially that of catalyst deactivation since nitrogen removal is often practiced simultaneously with sulfur removal on heavy feeds.

Flinn et al. (1962) showed that HDN proceeds rapidly with low-boiling charge stocks but becomes much slower as the boiling range increases. They observed that complete nitrogen removal is difficult even at 6000 psig for heavy vacuum gas oils and residua. Haensel et al. (1963) found progressively greater nitrogen removal while extending the pressure range to 24,000 psig. The reduced rate of HDN with higher-boiling feedstocks was attributed to the presence of aromatic nitrogen compounds and to the presence of aromatic hydrocarbons which can competitively adsorb on the catalyst. Haensel et al. (1963) suggested this when they found that nitrogen removal was lower in the presence of methylnaphthalene than in white oil.

It has been suggested that nitrogen removal from aromatic compounds takes place through an initial ring saturation step followed by ring cracking and subsequent nitrogen atom removal. McIlvried (1970) and Sonnemans (1973) confirmed this for pyridine HDN, and Goudriaan (1974) reported similar results for quinoline. The HDN reaction networks for pyridine and quinoline are shown in Figure 1. Table VII presents a summary of reported research on quinoline. Proposed rate limiting steps are given. Table VII indicates that the hydrogenation step (1)* is rate limiting at low temperatures ($<$ 320°C) and thermodynamically limiting at high temperatures ($>$ 320°C). At intermediate temperatures it appears that one of the hydrogenolysis steps (2 or 3) would be rate limiting. Using mass spectroscopy, Beugling (1971) identified a quinoline reaction product with a molecular weight of 257 and a chemical formula of $C_{18}H_{27}N$. The presence of this compound implies the occurrence of alkyl transfer reactions during the HDN of quinoline.

* Refer to Figure 1.

Pyridine Reaction Network. Sonnemans (1973)



Quinoline Reaction Network. Goudriaan (1974)

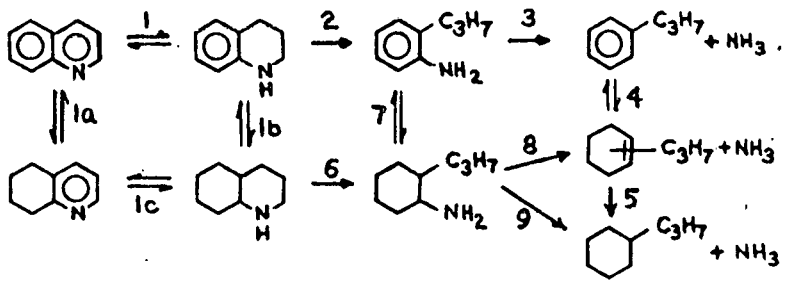


Figure 1. Hydrodenitrogenation Reaction Networks for Pyridine and Quinoline

TABLE VII*

RATE LIMITING STEPS IN THE HYDRODENITROGENATION OF QUINOLINE

Reference	Diluent	%w N in Feed	Catalyst	Temperature °C	Pressure, bar	Rate limited by step no.[a]
Flinn, et al. (1962)	Middle Distillate	0.5	Ni-W/Al_2O_3	315	70	1
Doelman & Vlugter (1963)	None	10.8	Co-Mo/Al_2O_3	300 350-400	80 80	1[b] 3
Ryffel (1960)	Refined Oil Fraction	2	Co-Mo/Al_2O_3	445	20-70	1[c]
Damon (1960)	Refined Oil Fraction	2	Co-Mo/Al_2O_3	385-400	20-70	3
Aboul-Gheit and Abdou (1972)	Paraffin Oil	0.5	Co-Mo/Al_2O_3	350-400	200	2

a) Step numbers correspond to Figure 1

* Goudriaan (1974)

Flinn et al. (1962) reported that quinoline is far more difficult to hydrodenitrogenate than aniline or n-butylamine, which are also basic, and indole, which is non-basic. Flinn et al. concluded that nitrogen compounds containing an aromatic-type heterocyclic ring are the more difficult to hydrodenitrogenate. Flinn et al. further concluded that the rate-limiting step in HDN is the saturation of aromatic-type, resonance-stabilized structures and that these structures can be present either as original components or as side-reaction products. Both quinoline and acridine fit this criterion.

There have been very few kinetic modeling studies on hydrodenitrogenation and most of these have concerned pyridine. Cox and Berg (1962) have reported that the HDN of both quinoline and acridine in toluene (and for 6-membered rings in general) follow pseudo first-order reaction kinetics. However, they found that many 5-membered ring nitrogen compounds follow second-order kinetics. Table VIII presents a summary of their results. As indicated in Table VIII, they found that the rate constants were a function of initial nitrogen compound concentration. This implies the

TABLE VIII

RATE CONSTANTS FOR THE HYDRODENITROGENATION OF A NUMBER OF NITROGEN-CONTAINING COMPOUNDS*

Compound	Initial Concentration Weight % N	K, 1/HR-Weight % N	95% Confidence Limits
Pyrrole	0.335	----------Non-linear----------	
Pyrrole	0.966	2.82	±0.418
Pyrrole	2.570	0.315	±0.0655
N-methyl pyrrole	0.303	9.93	±2.157
Pyrrolidine	0.3175	63.05	±3.22
Pyrrolidine	0.976	5.706	±0.435
Pyrrolidine	2.290	0.858	±0.00613
N-methyl pyrrolidine	0.306	25.50	±1.725
N-butyl pyrrolidine	0.295	42.63	±3.51
Indole	0.290	2.07	None

Compound	Initial Concentration Weight % N	K, 1/HR.	95% Confidence Limits
Pyrazine	0.305	13.74	±1.325
Pyridine	0.342	1.858	±0.226
Pyridine	0.980	0.576	±0.0324
Pyridine	2.210	0.214	±0.0177

TABLE VIII CONTINUED:

Compound	Initial Concentration Weight % N	K, 1/HR.	95% Confidence Limits
2-picoline	0.301	2.651	±0.616
3-picoline	0.319	1.040	±0.098
4-picoline	0.306	0.385	±0.081
2-ethyl pyridine	0.301	0.864	±0.093
4-ethyl pyridine	0.296	0.411	None
4-isopropyl pyridine	0.3005	0.125	None
2-benzyl pyridine	0.302	2.588	±0.162
4-benzyl pyridine	0.306	--------Non-linear--------	
2,4 lutidine	0.3045	0.272	±0.063
2,6 lutidine	0.296	1.800	±0.058
2,6 lutidine	1.000	0.718	±0.135
2,6 lutidine	2.450	0.492	±0.033
3,4 lutidine	0.291	0.0965	None
3,5 lutidine	0.291	0.279	None
3-ethyl-4-methyl pyridine	0.3655	0.114	±0.0765
2,4,6-collidine	0.307	0.512	None
Piperazine	0.307	--------Non-linear---------	
Piperidine	0.307	7.944	±1.01
2-methyl piperidine	0.302	9.56	±2.32
2,6-dimethyl piperidine	.302	6.92	±0.556
Quinoline	0.288	0.378	None
Acridine	0.2965	0.399	None

* Cox and Berg (1962)

need for inhibition terms in the kinetic model. Cox and Berg found that quinoline and acridine have similar rate constants and that these compounds are harder to hydrodenitrogenate than many others listed in Table VIII.

Flinn et al. (1963) also found that several organic nitrogen-containing compounds, including quinoline, indole, n-butylamine and aniline, followed pseudo first-order reaction kinetics. McIlvried (1970) summarized data for the hydrodenitrogenation of pyridine with a Langmuir-Hinshelwood kinetic model accounting for inhibition by ammonia and organic nitrogen-containing compounds. Sommemans et al. (1973) found that the following kinetic expression represented the rate of pyridine hydrogenation over an unsulfided cobalt-molybdenum oxide on alumina catalyst.

$$r = \frac{k p_P p_{H_2}^n}{p_{P_o}}$$

where

r = rate of pyridine hydrogenation

k = rate constant

p_{P_o} = initial pyridine partial pressure

p_P = pyridine partial pressure

p_{H_2} = hydrogen partial pressure

n = constant = 1.0 at 250°C
1.5 at 300-375°C

The above kinetic expression suggests that the strength of adsorption of pyridine and its hydrogenation products are equal. Sonnemans et al. (1973) found similar results for sulfided catalysts. However, the validity of this claim is unclear. Most industrial hydrodenitrogenation operations take place in the presence of sulfur compounds and with a presulfided catalyst.

Also, at the present time it is unclear which catalyst is best for hydrodenitrogenation operations. Many industrial operations where hydrodesulfurization and hydrodenitrogenation take place simultaneously use a cobalt-molybdenum supported on alumina catalyst. However, several commercial catalyst companies, such as American Cyanimid, have developed nickel-molybdenum and nickel-tungsten catalysts specifically for hydrodenitrogenation.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

A. Reactor System

This section includes a summary of the reactor system and operation. Also included is the catalyst sulfiding procedure. Both a 300 cc and a 1000 cc autoclave batch reactors were used for the hydrodenitrogenation (HDN) studies. Figure 2 presents a schematic of a reactor system. Its features include a catalyst injection system and gas sampling capabilities. Porous stainless-steel filters (0.5 μm porosity) were used as a gas sparger and as a filter for securing liquid samples.

Operation of the unit was as follows. The solvent medium, white oil, and nitrogen-containing compound were initially placed in the reactor. In the quinoline studies quinoline was held in the loading device. The oil was purged of oxygen, pressured with hydrogen gas and heated to reaction conditions. A slurry of catalyst and white oil was kept in the load-

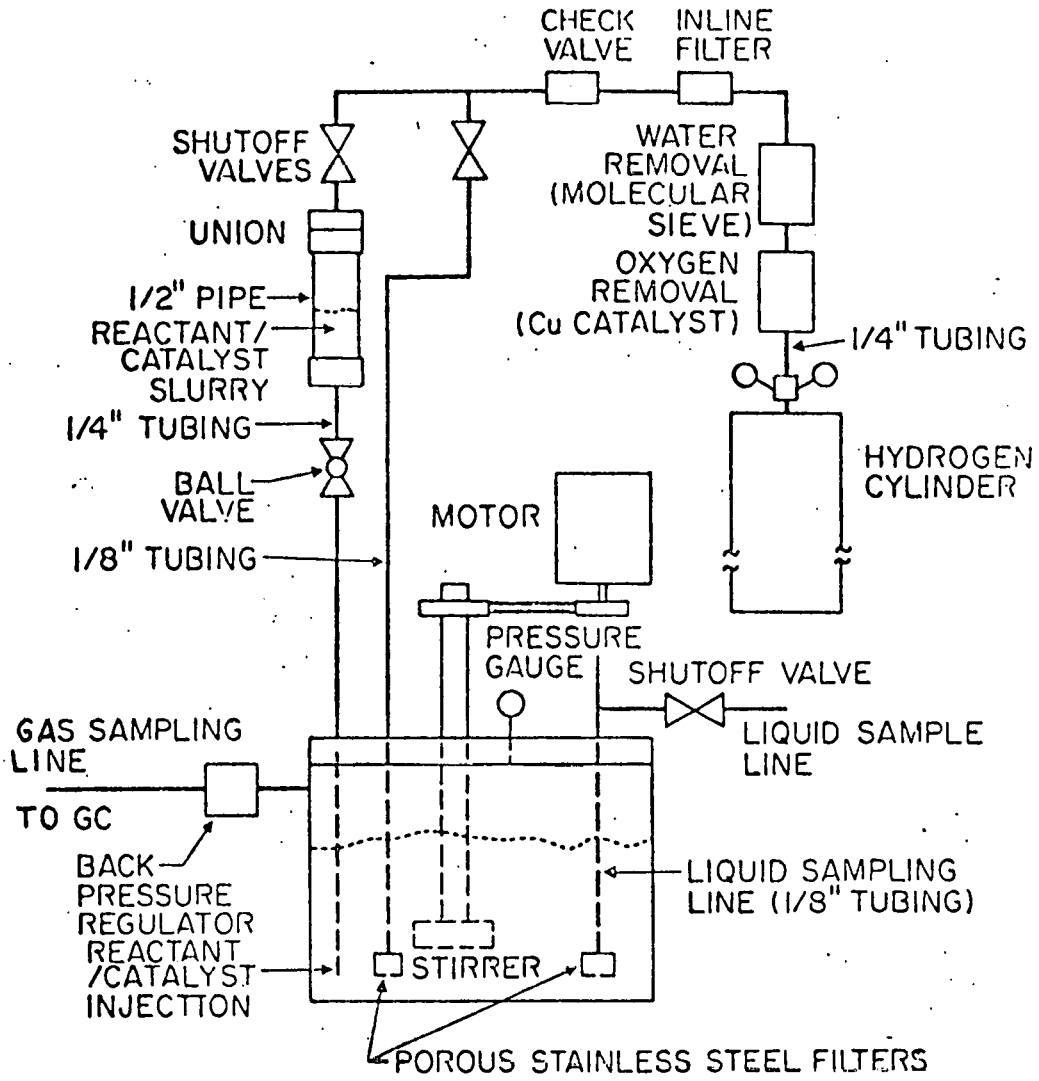


Figure 2. Schematic of High-Pressure Autoclave Batch Reactor

ing device to this point. When reaction conditions had stabilized, the slurry was injected into the reactor using hydrogen gas as a driving force. Liquid samples passed through a porous stainless steel filter, which was used to inhibit the loss of catalyst, and were collected downstream of a valve used to break pressure. The temperature was controlled and monitored using the thermowell thermocouple immersed in the reaction mixture from the autoclave bulkhead. A Thermoelectric Model 800 temperature controller was used to control the temperature.

Most commercial hydroprocessing catalysts consist of a transition metal or metals, such as cobalt and molybdenum, impregnated on an alumina support. The metals are present as oxides. It is standard procedure industrially to presulfide the catalyst before use to convert the metal oxides to sulfides. All catalysts used in this research were presulfided according to the following procedures. The catalyst was presulfided in a Pyrex glass tube for 2 hours at 325°C or 400°C. A mixture of 10% H_2S in H_2 flowed over the catalyst such that it saw approximately 10 times the stoichiometric amount of sulfur necessary for complete conversion of the metal oxides on the catalyst to the sulfidic form. The catalyst was then

cooled and placed in the reactor loading device.

B. Catalyst and Reaction Compound Properties

Either white oil or normal-hexadecane was used as a reaction solvent medium. White oil (Parol 70 TECH) is a white mineral oil obtained from Penreco. White oil is a natural stock consisting of C_{18}-C_{36} (193-260°C) paraffinic and naphthenic hydrocarbons which have been hydrotreated and oleum treated. Typical properties are presented in Table IX. White oil contains essentially no aromatics or nitrogen and sulfur compounds. Normal-hexadecane was obtained from Columbia Organic Chemicals Company. Typical properties for normal-hexadecane are presented in Table X.

Quinoline and acridine were obtained from Columbia Organic Chemicals Company. Typical properties are shown in Table XI.

Table XII presents a summary of typical catalyst properties obtained from manufacturers' brochures.

TABLE IX

TYPICAL PROPERTIES OF WHITE OIL*

Viscosity at 100°F (37.8°C)	9.7/12.2 centiposes
Specific Gravity, 60°/60°F (15.6°C)	0.840/0.855
77°/77°F (25°C)	0.834/0.849
Flash Point, °F ASTM	330
Pour Point, °F ASTM	15
Refractive Index, n_D^{20}	1.4635
UV Adsorbance	1%
Initial Boiling Point, °C	193 minimum
Distillation End Point, °C	260 maximum
Color	colorless

* Supplied by Manufacturer

TABLE X

TYPICAL PROPERTIES FOR NORMAL-HEXADECANE*

Molecular Weight	226.45
Specific Gravity	$0.774\ \frac{20°}{4}$
Melting Point, °C	18.5, 16.2
Boiling Point, °C	287.5
Purity (from Manufacturer)	99%

---

* Dean (1973)

TABLE XI

TYPICAL PROPERTIES FOR QUINOLINE AND ACRIDINE*

	Quinoline	Acridine
Purity (from Manufacturer)	99%	99%
Molecular Weight	129.16	179.22
Melting Point, °C	-15.6	110-1
Boiling Point, °C	237.1^{747mm}	346
Specific Gravity	$1.095^{20°}$	-------

* Dean (1973)

TABLE XII

TYPICAL CATALYST PROPERTIES

	Cyanimid HDS-9A	NALCO NT-550	Harshaw 4303 E	Harshaw 4301 E	Cyanimid HDS-16A
Composition, wt %	NiO, 3.0-4.0	WO_3, 22.0	WO_3, 18	WO_3, 18	MoO_3, 12.2
	MoO_3, 17.5-18.5	NiO, 5.1	NiO, 6	NiO, 6	CoO, 5.7
	Na_2O, 0.04	Al_2O_3			Na_2O, 0.03
	Fe, 0.05				Fe, 0.04
Surface area, m^2/g	--------	250	152	228	---------
Pore volume, cc/g	--------	0.5	0.54	0.37	---------

C. Analytical Procedures

1. Introduction

There were two types of reaction products which required quantitative analysis. These were the reactor off-gas and liquid reaction products. The off-gas consisted of hydrogen with trace amounts of light hydrocarbons (C_1 to C_5) and of ammonia and hydrogen sulfide. The liquid reaction products consisted of organic nitrogen compounds in white oil or in normal-hexadecane. Hydrocarbon reaction products in the liquid samples were not analyzed.

While gas chromatographic technology for the analysis of the off-gas is well developed, an adequate and convenient analytical scheme needed to be developed for the analysis of the liquid products with nitrogen-containing compounds. Gas chromatography (GC) and liquid chromatography (LC) were investigated. It was found that GC with a nitrogen-specific detector provided suitable means for quantitative analysis of nitrogen-containing liquid reaction products.

2. Off-Gas Analysis

An F and M Laboratory Model 700 GC was used

for the analysis of the off-gas reaction products. Columns and conditions are given in Table XIII. The main purpose of the off-gas analysis was to ensure that the solvent was not being cracked significantly and to measure the hydrogen sulfide content of the gas phase.

3. Liquid Reaction Products Analysis - A Comparison of Gas Chromatography and Liquid Chromatography

The search for adequate and convenient quantitative analysis of liquid reaction products containing nitrogen centered on studying the feasibilities of liquid chromatography (LC) and gas chromatography (GC). Comments and suggestions were secured from various companies and organizations including Oak Ridge National Laboratory, Gulf Oil, American Cyanimid, E. I. duPont de Nemours, the Pittsburgh Energy Research Center, Hewlett-Packard, Perkin-Elmer and Tracor. After several white oil samples doped with organic sulfur or nitrogen-containing compounds were analyzed by both LC and GC, it was determined that GC with a nitrogen specific detector and a sulfur specific detector would provide suitable means for quantitative analysis of heteroatom-containing liquid reaction products.

TABLE XIII

GC CONDITIONS FOR ANALYSIS OF OFF-GAS REACTION PRODUCTS

		Column A	Column B
Compounds Analyzed (with relative retention times)	methane	0.22	0.33
	ethane	0.29	0.43
	propane	0.46	0.61
	butane	1.00	1.00
	ammonia	----	3.87
	hydrogen sulfide	0.47	0.76
Carrier Gas Flowrate, cc/min		Helium 20.3	Helium 18.9
Detector		Thermal Conductivity (TC)	TC
Current, ma		205	205
Temperature, °C		204	204
Temperature, °C			
Sampling value		70	70
Column		ambient	119
Injection Port		160-165	160-165

GC: F&M Laboratory Model 700
Column A: n-Octane coated on Porasil C (Waters Associates)
Column B: Poropak T
80-100 mesh
8' X 1/8" stainless steel column

Figures 3, 4, 5 and 6 present gas chromatograms run on a Perkin-Elmer Model 3920 GC. Chromatograms in Figures 3 and 4 were run using the FID (flame ionization detector) mode. Figure 3 shows a pure white oil sample while Figure 4 shows a sample of 1.3 wt% technical grade quinoline in white oil. Figure 5 presents a gas chromatogram of 1.3 wt% quinoline in white oil run on the nitrogen specific detector mode. All of the peaks shown in Figure 5 are due to organic nitrogen-containing compounds with essentially no interference from the white oil background. A comparison of Figures 4 and 5 shows that complete baseline resolution of the complex mixture of hydrocarbons in white oil is not necessary for the quantitative analysis of nitrogen-containing compounds. Figure 6 shows a gas chromatogram of a sample of 0.25 wt% dibenzothiophene in white oil run on a Dexsil SCOT (Support coated open tubular column) column with monitoring both by the sulfur specific detector (FPD-flame photometric detector) and FID. Figure 6 indicates that there was complete baseline resolution of sulfur-containing compounds. A comparison of Figures 3 and 6 indicates that the SCOT column provides a better separation of the white oil.

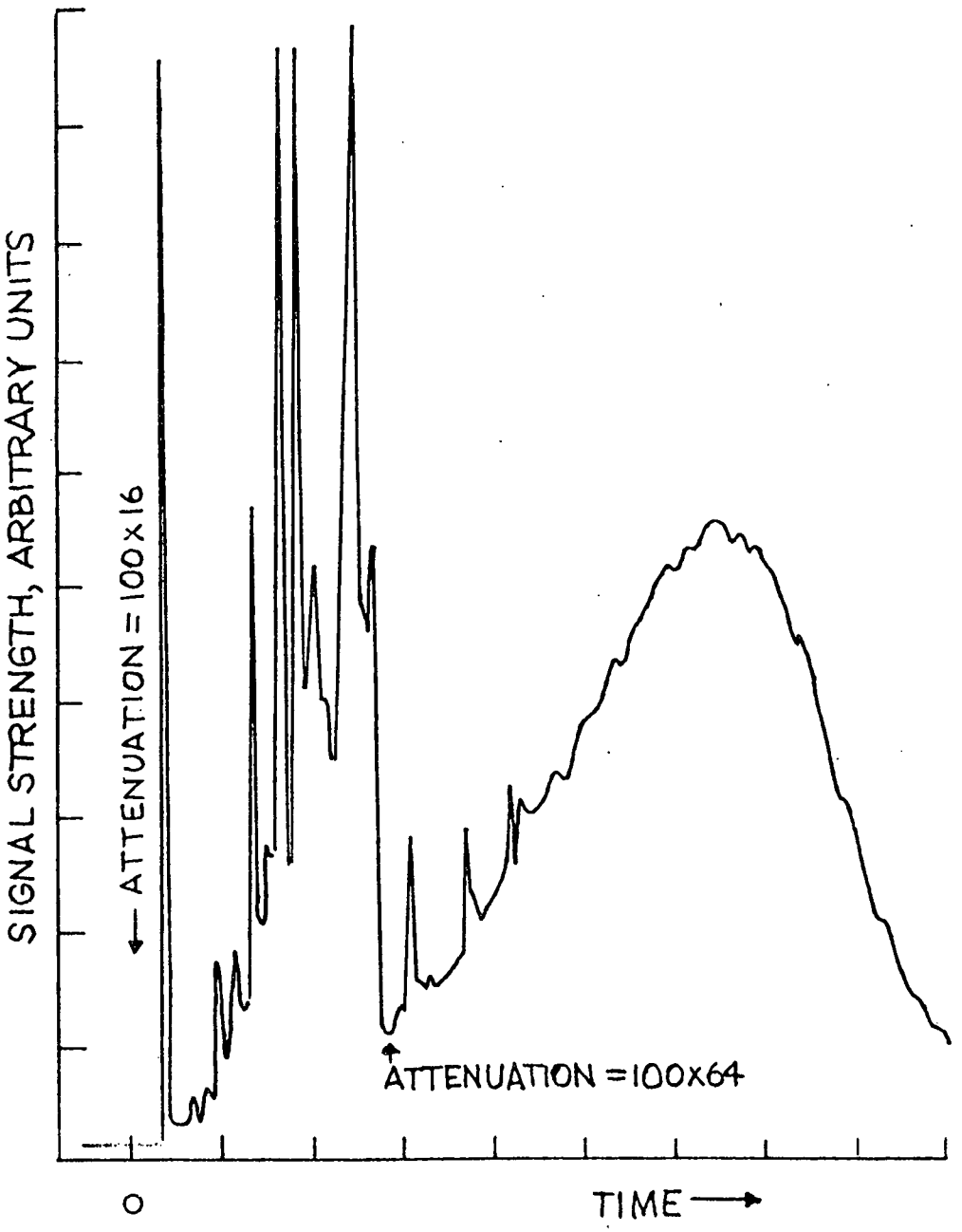


Figure 3. Gas Chromatogram of White Oil obtained with a Flame Ionization Detector: Perkin-Elmer GC, 6 ft. OV-17 on Chromasorb Q glass column. Temperature programmed 120-280°C at 8°C/min. 0.5 ul injected.

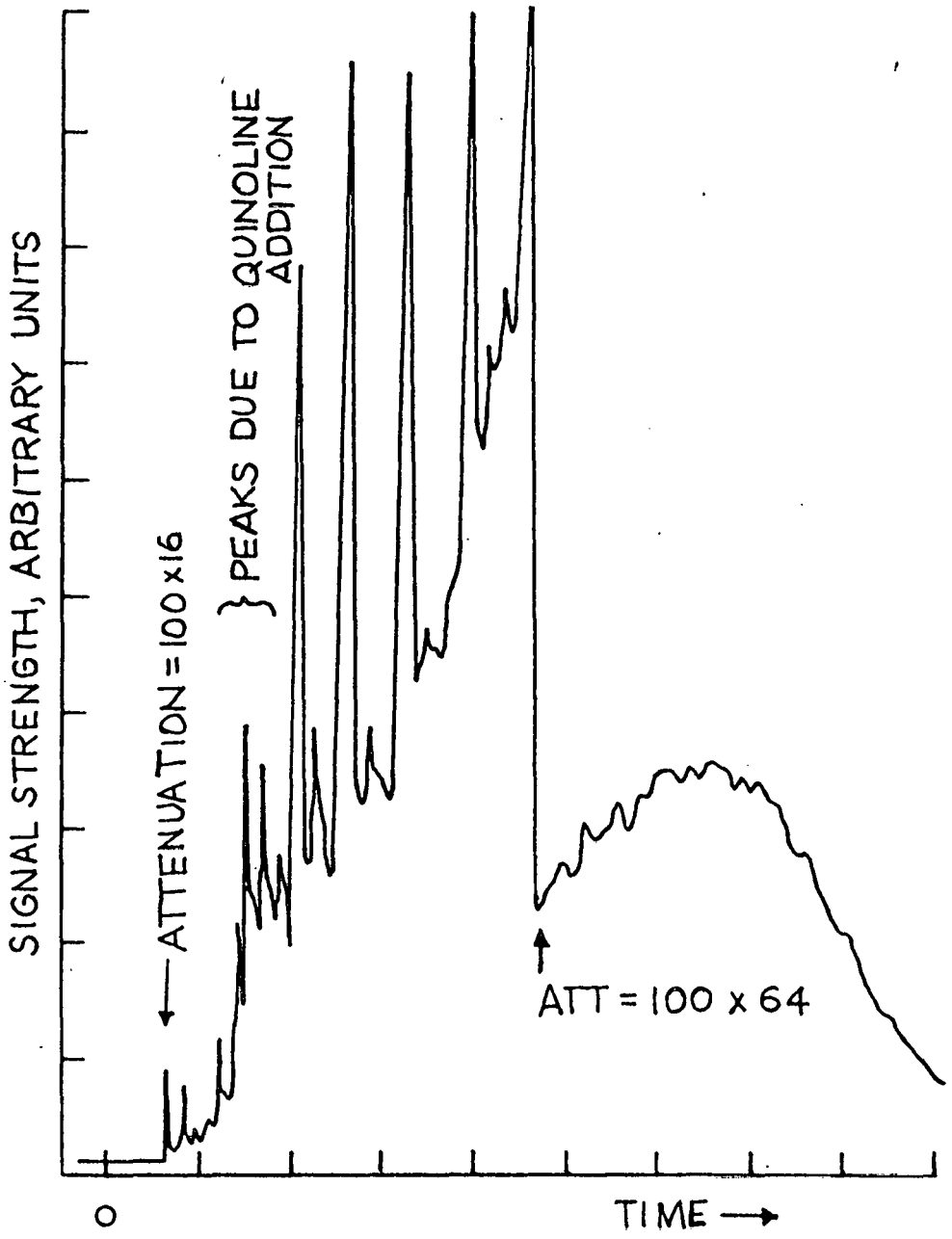


Figure 4. Gas Chromatogram of White Oil with 1.3 wt% Technical Grade Quinoline obtained with a Flame Ionization Detector: operating conditions same as for Figure 3.

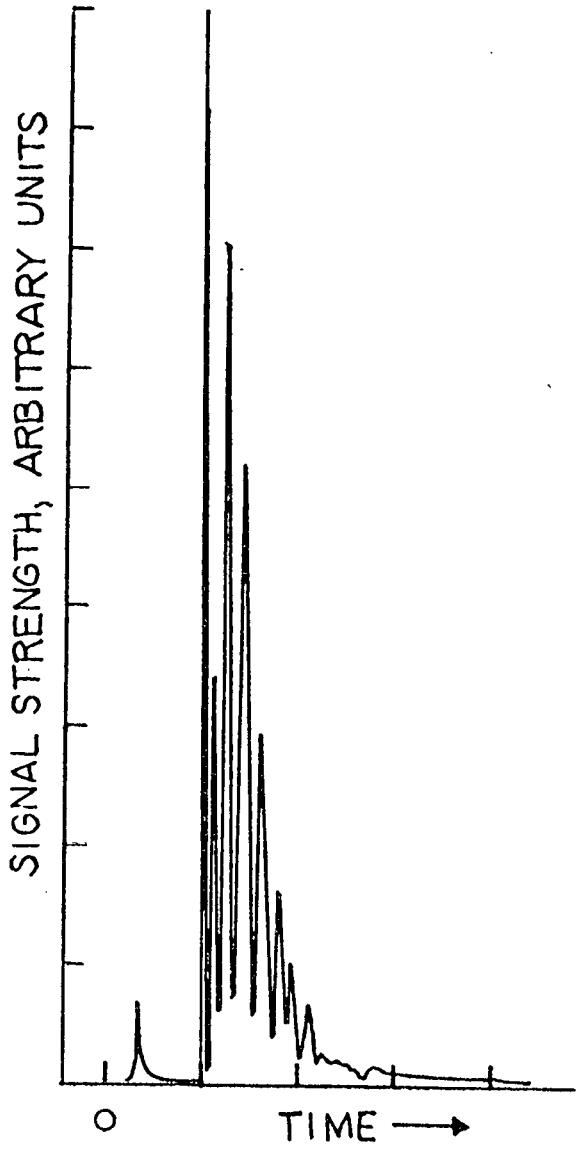


Figure 5. Gas Chromatogram of White Oil with 1.3 wt% Technical Grade Quinoline obtained with a Perkin-Elmer Nitrogen Specific Detector: operating conditions same as for Figure 3.

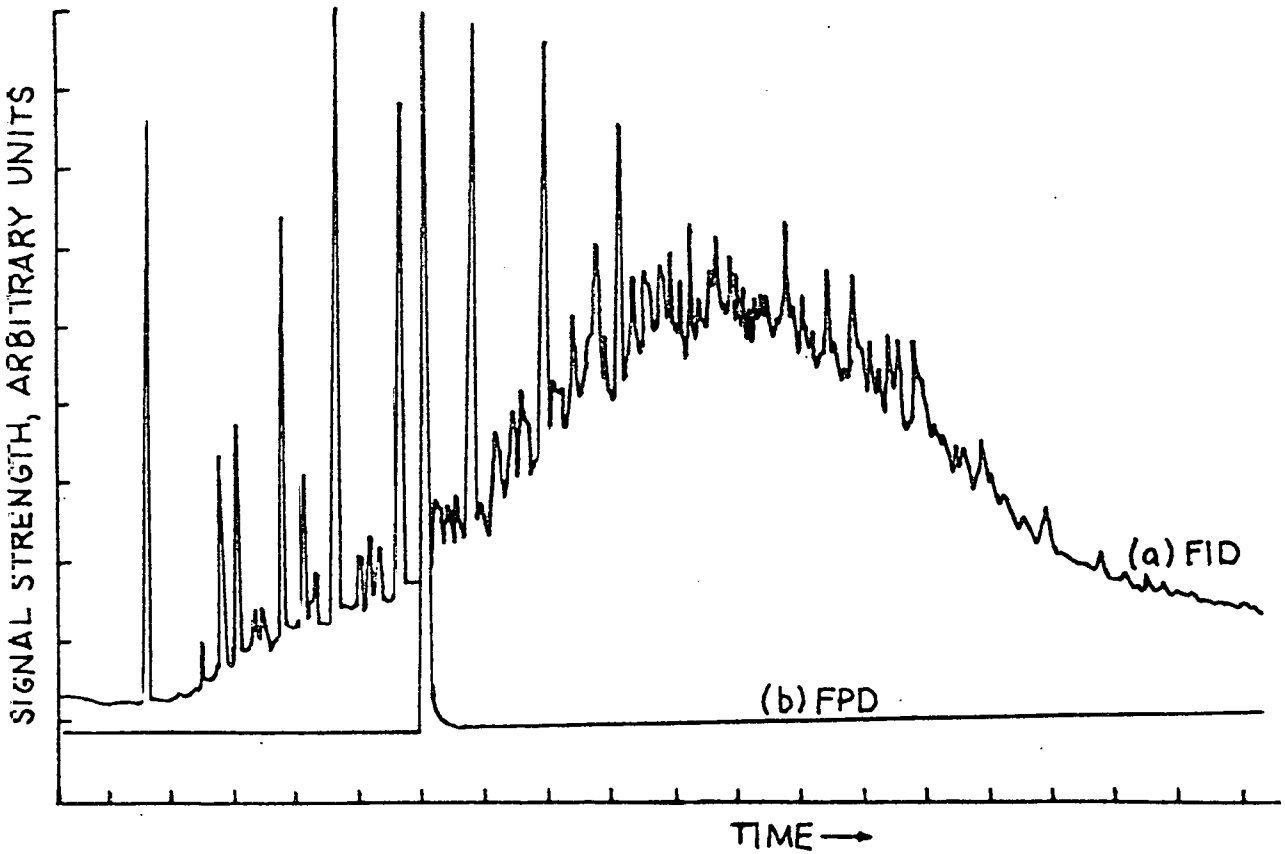


Figure 6. Gas Chromatogram of Dibenzothiophene in White Oil obtained with a Flame Ionization Detector (Curve a) and with a Sulfur Specific Detector (Curve b): Perkin-Elmer GC with a Dexsil SCOT column 0.02 in. by 50 ft., temperature programmed 150-300°C at 4°C/min.

Figure 7 presents a chromatogram of 1.3 wt% technical grade quinoline in white oil run on a Perkin-Elmer Model 601 liquid chromatograph with an UV (ultraviolet) detector. A comparison of Figures 4 and 7 indicates that the GC produced better resolution than LC. It is important to note that while the UV detector is sensitive to unsaturated compounds, it is not sensitive to saturated species. This is a definite limitation, especially to the HDN work, since it is often reported that the reaction network of aromatic nitrogen compounds involves saturation of the ring structure as the first step.

Economics were also considered in choosing LC over GC. The purchase cost of an LC is 50 to 100% higher than that of a GC. Expensive high purity solvents make the operating costs of an LC quite high. LC technology is not as far advanced as GC technology. This leads to a poorer quantity of applications literature available for the LC.

4. Analysis and Identification of Nitrogen-Containing Reaction Products of Quinoline and Acridine

A Perkin-Elmer Model 3920B gas chromatograph with a Perkin-Elmer nitrogen specific detector was used

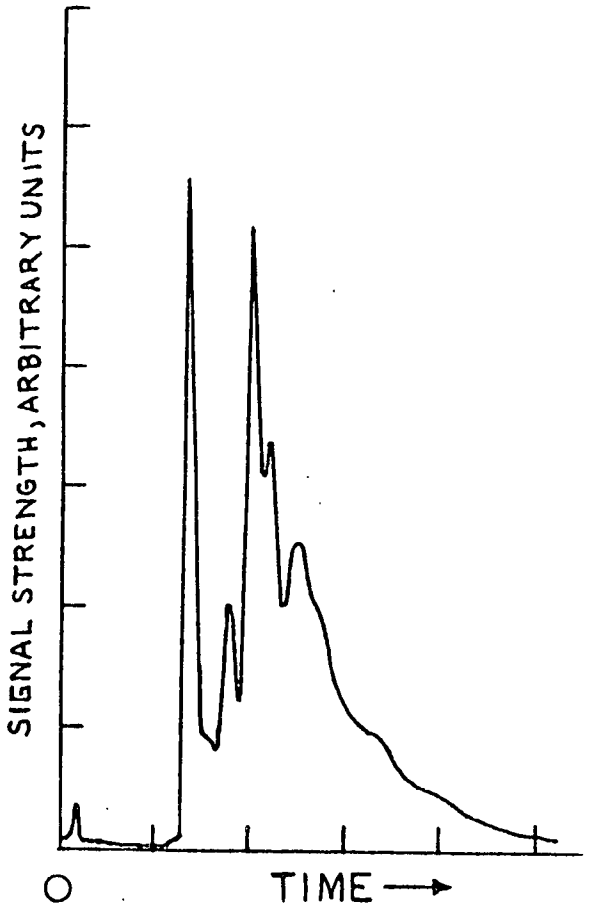


Figure 7. Liquid Chromatogram of 1.3 wt% Technical Grade Quinoline in White Oil: Perkin-Elmer Model 601 LC, ultraviolet detector, OD SIL-X-IRP column (2.54 mm by 0.5 m), 55°C isothermal, 40% MeOH in H_2O solvent.

to quantify the nitrogen-containing reaction products of quinoline and acridine. The detector response was monitored with a Columbia Scientific Industries Supergrator-2 integrator. The response of quinoline was found to be linear over the concentration range of interest as shown in Figure 8. A list of relative response factors for some nitrogen-containing compounds are shown in Table XIV. Except for aniline the response factors of the nitrogen compounds differ by no more than 25%. Since all the nitrogen-containing reaction products for quinoline or acridine were not available commercially, it was assumed that the response factors for the nitrogen-containing reaction products were the same as that for the starting nitrogen compound.

Chromatographic conditions for the analysis of quinoline products and of acridine products are given in Table XV. Many other columns and conditions were tried but were found to be unsuccessful for one or more reasons. Details are presented in Appendix F. A recurring problem throughout this research was the stability of the chromatographic system. The high molecular weight reaction medium (white oil) and possibly absorption of nitrogen-containing compounds on the column

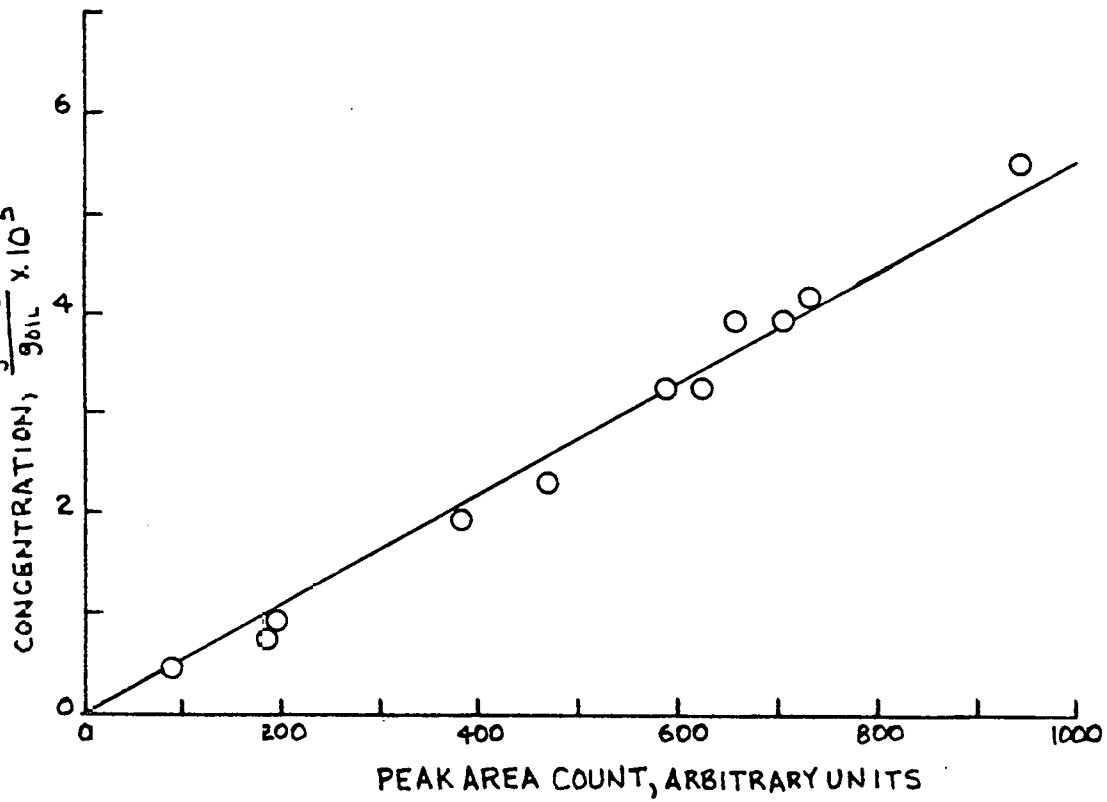


Figure 8. Calibration Curve for Quinoline: operating conditions given in Table XV.

TABLE XIV

RELATIVE RESPONSE FACTORS FOR VARIOUS NITROGEN-CONTAINING COMPOUNDS

Compound	Relative Response Factor
Acridine	1.00
1,2,3,4-tetrahydroquinoline	0.987
sym-octahydroacridine	0.882
n-propylaniline	0.862
Quinoline	0.804
Aniline	1.364

$$\text{RELATIVE RESPONSE FACTOR} = \frac{[\text{CONCENTRATION}]_i / [\text{PEAK AREA}]_i}{[\text{CONCENTRATION}]_{\text{ACRIDINE}} / [\text{PEAK AREA}]_{\text{ACRIDINE}}}$$

CONDITIONS: PE3920B GC
Nitrogen Specific Detector

Column: 5' X 1/8" Glass Apiezon L (2% KOH) Column, 80-100 mesh, 195°C Isothermal

Injector: 300°C
Interface: 300°C
Carrier Gas: Helium at 30 cc/min

TABLE XV

GAS CHROMATOGRAPH CONDITIONS FOR THE ANALYSIS OF QUINOLINE AND ACRIDINE NITROGEN-CONTAINING REACTION PRODUCTS

	Quinoline	Acridine
Column	6' X 1/8" Chromosorb 103	5' X 1/8" Glass Apiezon (2% KOH)
Mesh Size	60-80	80-100
Carrier Gas	Helium	Helium
Flowrate, cc/min	12-20	30
Nitrogen Detector Settings Current Setting	5.0-6.0	6.0
H_2 Pressure, psig	5.0	5.0
Air Pressure, psig	50	50
Injector Temperature, °C	250	300
Interface Temperature, °C	300	300

were blamed for this instability. It was felt that the high temperatures required to elute the white oil and the large amount of white oil which passed through the detector along with the nitrogen compounds contributed to the poor stability. Response factors changed as much as 50% on a given day and changed possibly an order of magnitude from day to day. For the quinoline and acridine experiments standards were run after every 3 to 5 samples to overcome this problem.

A mass spectrometer (HP 5930A) - gas chromatograph (HP 5750) system was used to identify the nitrogen-containing reaction products of acridine. The mass spectrometer conditions are given in Table XVI. The chromatographic column and conditions were similar to those given for acridine in Table XV. A thermal conductivity detector was used to monitor the gas chromatograph effluent. Detailed mass spectroscopic procedures are presented in Appendix H . The procedure for extracting the nitrogen-containing compounds is presented in Appendix G.

TABLE XVI

MASS SPECTROMETER CONDITIONS

Ionization Voltage	70 (ev)
Pressure	2×10^{-6} torr
Source temperature	100°C
Chromatograph-Spectrometer	
Interface Temperature	200°C

CHAPTER III

RESULTS

A. Preliminary Experiments: Hydrodenitrogenation of Quinoline

This work was performed within the ERDA Hydroprocessing Contract No. E(49-18)-2028 at the University of Delaware. Principal experimenters were the author and Dr. Stuart Shih. The hydrodenitrogenation of quinoline was studied initially to evaluate the performance of two autoclave reactor systems and to evaluate the relative catalyst activity of several commercially available hydroprocessing catalysts. In all of this quinoline work the catalysts were presulfided, but no CS_2 was added to the reaction medium.

1. Activity of Blank Reactor

Two runs without catalyst were performed by Dr. Shih to analyze any intrinsic activity of the autoclave reactor system. One experiment had a feed of quinoline in white oil and another had 1,2,3,4-tetrahydroquinoline in white oil. The reaction condi-

tions were 342°C and 500 psig. These experiments showed that the rate of reaction without catalyst was very slow. The total nitrogen removal over a four hour period was less than 5%. The total nitrogen removal would be about 50% in 6 hours at these conditions if catalyst were present.

2. Reactor Reproducibility

Two quinoline in white oil experiments were made to evaluate reactor reproducibility between the 300 cc and 1000 cc autoclave reactors. These runs were made with Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) catalyst. Reaction conditions are shown in Table XVII. These runs indicated that quinoline is rapidly hydrogenated to 1,2,3,4-tetrahydroquinoline and that o-propylaniline and decahydroquinoline are also formed. Figure 9 shows the concentration ratio of tetrahydroquinoline to quinoline plotted versus time for the two experiments. The ratio lines-out at a constant value of about 7.5 indicating that the compounds are in equilibrium. An experiment starting with 1,2,3,4-tetrahydroquinoline established the same constant concentration ratio confirming equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline (Shih, 1976).

TABLE XVII

REACTION CONDITIONS FOR REACTOR REPRODUCIBILITY EXPERIMENTS

Temperature	342°C
Pressure	500 psig
Reactant	0.85 wt% quinoline in white oil
Autoclave stirring speed	1250 rpm
Catalyst type	Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A)
Catalyst Particle size	100-140 mesh (125 μm)
Catalyst Concentration	2g/500 cc oil
Catalyst Presulfided at 325°C	
No CS_2 added to reaction medium	

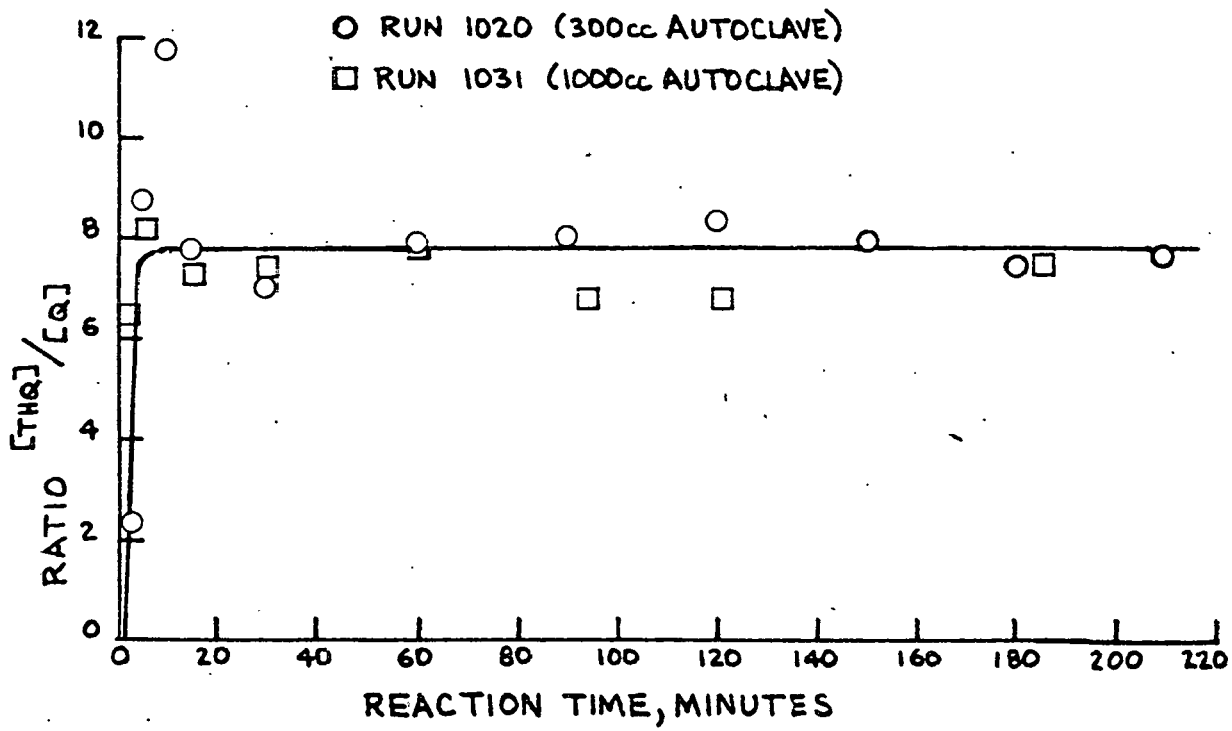


Figure 9. Concentration Ratio of 1,2,3,4-tetrahydroquinoline to Quinoline for the Reactor Reproducibility Experiments: Quinoline Hydrodenitrogenation at 342°C and 500 psig; Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) catalyst.

Reaction reproducibility was evaluated through comparison of pseudo first-order rate constants for the disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline. Figure 10 presents a plot of the logarithim of the quinoline plus tetrahydroquinoline concentration versus time. A least squares analysis produced the rate constants and correlation coefficients* shown in Figure 10. The two sets of data produced rate constants which differed by less than 2%. Figure 11 presents a pseudo first-order kinetic analysis for total nitrogen removal for the reproducibility experiments. The rate constants agreed to two significant figures and the coefficients of correlation indicated a reasonably good fit of the data. Detailed mathematics on the kinetic analysis are presented in Appendix A, and detailed concentration profile data are given in Appendix B.

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* The coefficient of correlation is the ratio of unexplained variation to the total variation. Therefore, if the data fit the model perfectly, the correlation coefficient is $\pm$ 1.0.

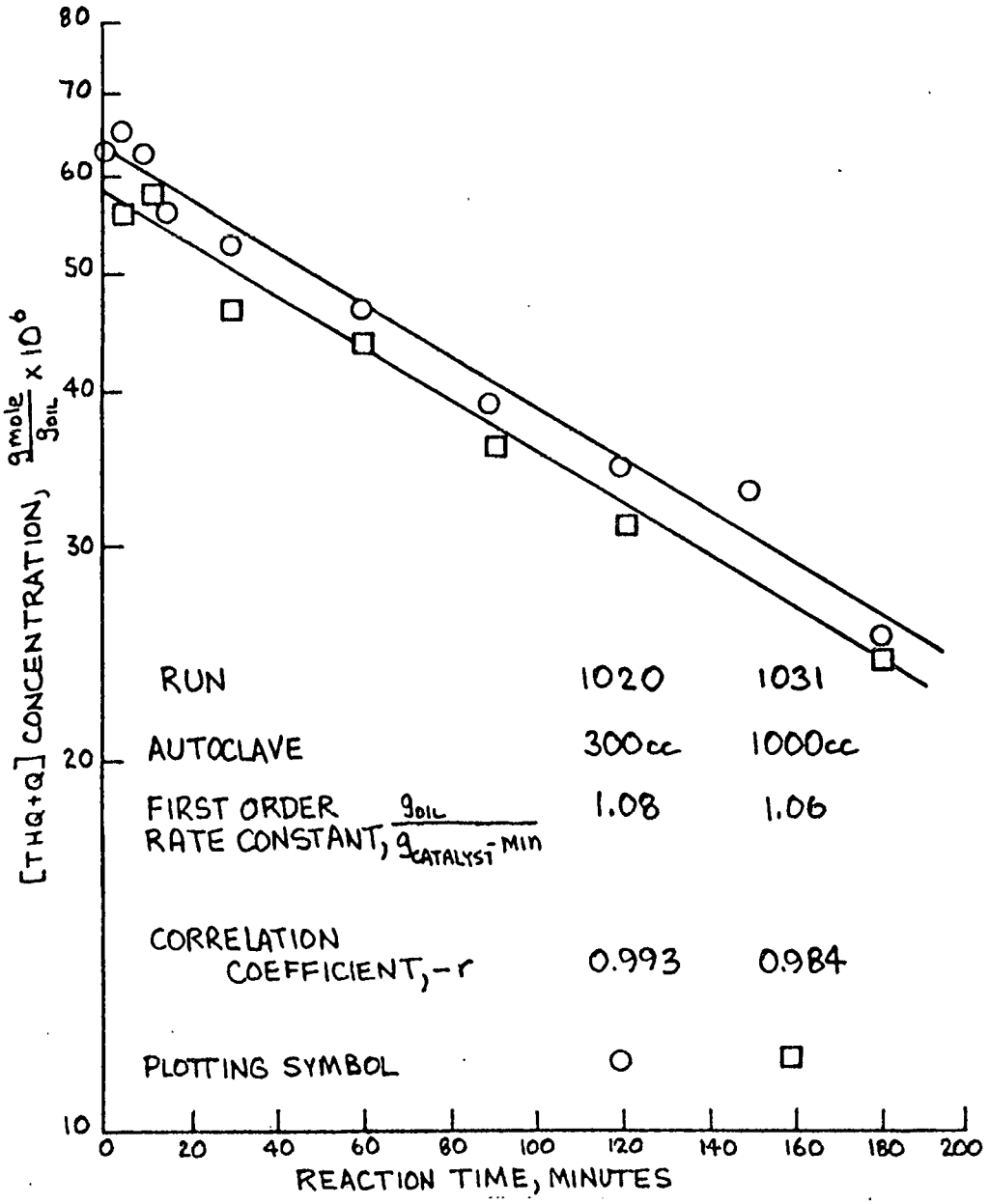


Figure 10. Pseudo First-order Kinetic Analysis of the lumped group of Quinoline plus 1,2,3,4-tetrahydroquinoline for the Reactor Reproducibility Experiments: Quinoline Hydrodenitrogenation at 342°C and 500 psig Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

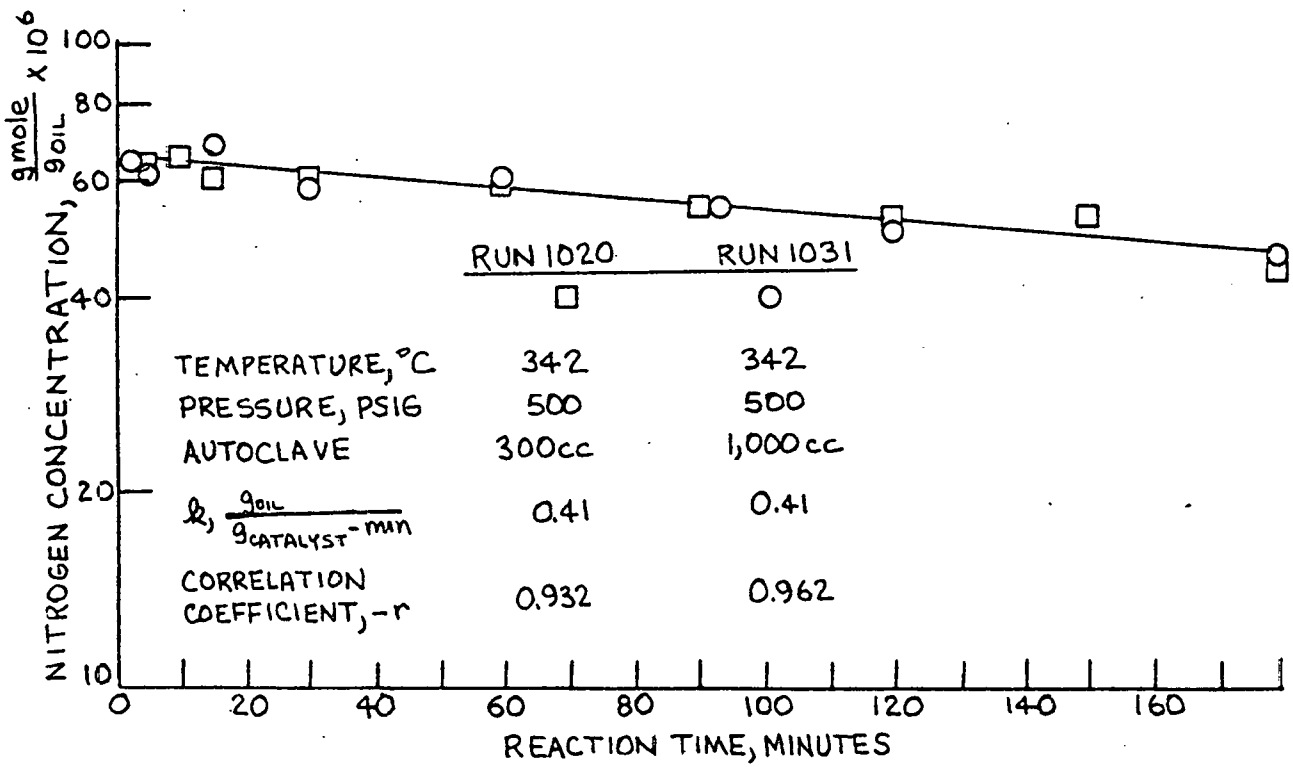


Figure 11. Pseudo First-order Kinetic Analysis of Total Nitrogen Removal for the Reactor Reproducibility Experiments: Hydrodenitrogenation of Quinoline at 342°C and 500 psig; Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

3. Evaluation of Mass Transfer Effects

The objective of these experiments was to determine the effect of the catalyst particle size and thus illustrate the presence or absence of significant mass transfer effects on the rate of hydrodenitrogenation of quinoline in white oil at 342°C and 500 psig. Ni-Mo/Al_2O_3 (American Cyanimid HDS-16A) catalyst was used in this study, and its particle size was varied in the range of 48 to 200 mesh (275 μm to 74 μm). Reaction conditions are presented in Table XVIII. The rate of hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline and the rate of disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline were used as a basis for studying the effect of catalyst particle size.

Three experiments were made with different catalyst particle sizes. Figure 12 presents the effect of catalyst particle size on the rate of hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. Figure 12 shows that equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline was more slowly attained for the larger (275 μm) catalyst particle size (Run 1016) than for the smaller (90 μm) catalyst

TABLE XVIII

REACTION CONDITIONS FOR MASS TRANSFER EFFECTS STUDY

Temperature		342°C
Pressure		500 psig
Catalyst type		Co-Mo/Al_2O_3 (American Cyanimid HDS-16A)
Catalyst Concentration		2g/500 cc oil
Catalyst Presulfided at 325°C		
No CS_2 added to reaction medium		
Reactant		0.85 wt% quinoline in white oil
Catalyst Particle Size	Run 1015	100-140 mesh (125 μm)
	1016	48- 60 mesh (275 μm)
	1017	140-200 mesh (90 μm)
Stirring Speed	Run 1015	750 rpm
	1016	1250 rpm
	1017	1250 rpm

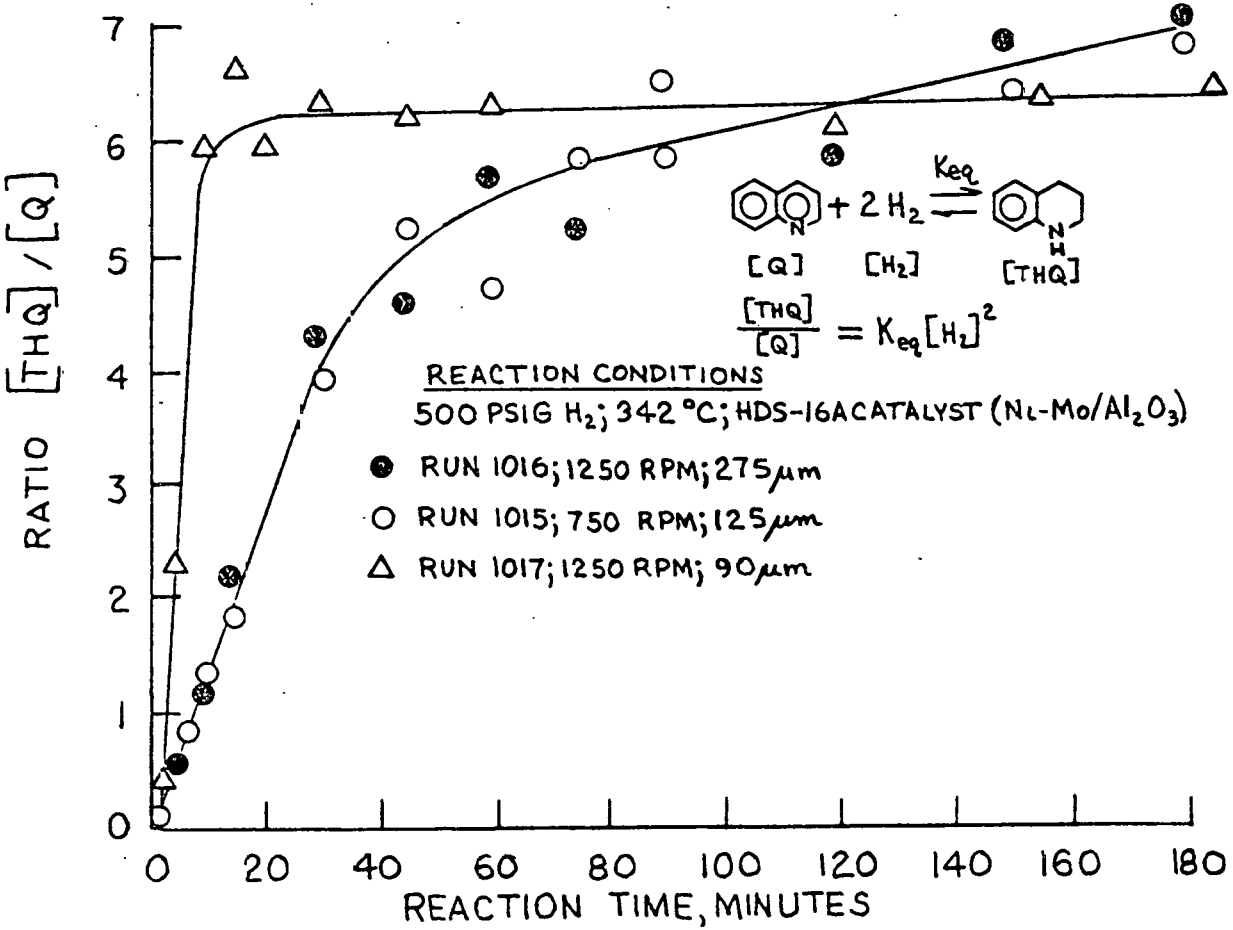


Figure 12. Effect of Catalyst Particle Size on the Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline.

particle size (Run 1017). The intermediate (125 μm) catalyst particle size (Run 1015) was run at a lower stirring speed. This experiment indicated that significant liquid mass transfer resistances are present since Figure 12 indicates that the rate of hydrogenation for Run 1015 (125 μm) was no faster than that for Run 1016 (275 μm), which had a larger catalyst particle size.

Figure 13 shows the observed pseudo first-order kinetic behavior for Runs 1016 (275 μm) and 1917 (90 μm), and Table XIX presents the first-order rate constants for all three experiments. Figure 13 indicates that pseudo first-order kinetics fit the data very well. Table XIX shows that the rate constants for Run 1016 (275 μm) and 1017 (90 μm) differ by more than 20%. Effectiveness factor calculations based on these kinetics indicate that the effectiveness factors for all three experiments were 1.0. Detailed calculations are presented in Appendix C. Detailed concentration profiles for the catalyst particle size survey are presented in Appendix D.

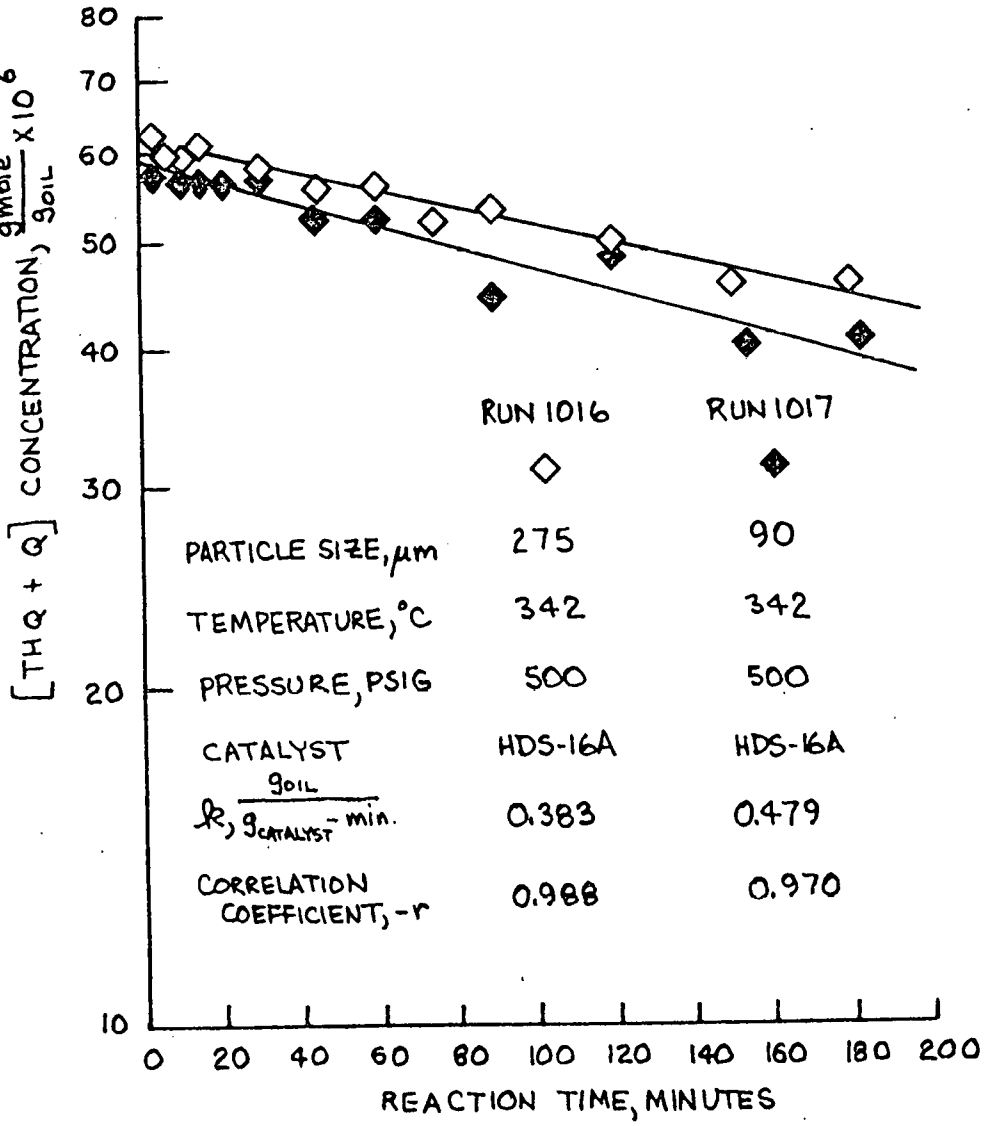


Figure 13. Effect of Catalyst Particle Size on the Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline.

TABLE XIX

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF THE LUMPED GROUP OF QUINOLINE PLUS 1,2,3,4-TETRAHYDROQUINOLINE

Run	Catalyst Particle Size, μm	$K_{THQ} + Q$, $\frac{g_{oil}}{g_{catalyst}\text{-min}}$
1016	275	0.383
1015	125	0.319
1017	90	0.479

4. Catalyst Survey

The objective of this survey was to determine the relative activity of the more common commercially available hydrotreating catalysts and to choose the most active one based on the hydrodenitrogenation of quinoline in white oil at 342°C and 500 psig. The catalyst types included Co-Mo/Al_2O_3 (American Cyanimid HDS-16A), Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A), Ni-W/Al_2O_3 (Harshaw Ni4303 and NALCO NT-550), and Ni-W/Al_2O_3-SiO_2 (Harshaw Ni4301). Reaction conditions are presented in Table XX.

The reaction data were analyzed on the basis of the disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline. Pseudo zero-order and pseudo first-order kinetics were considered, and a least squares analysis was used as a basis for comparison. Table XXI presents a summary of this analysis. Table XXII presents a comparison of the predicted initial quinoline concentration by the two kinetic models versus the actual loaded quinoline concentration.

Table XXI, along with Table XXII, indicates

TABLE XX

REACTION CONDITIONS FOR CATALYST SURVEY

Temperature	342°C
Pressure	500 psig
Catalyst concentration	2g/500 cc oil
Catalyst presulfided	
No CS_2 added to reaction medium	
Reactant	0.85 wt% quinoline in white oil
Autoclave stirring speed	1250 rpm

TABLE XXI

KINETIC MODEL ANALYSIS FOR CATALYSTS EVALUATION

Catalyst	Run No.	First Order Rate Constant, $k_{THQ + Q}$, $\frac{g_{oil}}{g_{catalyst}\text{-min}}$	Correlation Coefficient, -r	Zero-Order Rate Constant X 10^5, $\frac{g\ mole\ (Q + THQ)}{g_{oil}\text{-}g_{catalyst}\text{-min}}$	Correlation Coefficient, -r
Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A)	1020	1.08	0.993	4.42	0.979
Ni-W/Al_2O_3 (UOP-LCO HT-550)	1023	0.950	0.997	4.10	0.985
Ni-W/Al_2O_3 (Harshaw Ni4303)	1022	0.687	0.976	3.41	0.961
Ni-W/SiO_2-Al_2O_3 (Harshaw Ni4301)	1021	0.578	0.989	2.86	0.978
Co-Mo/Al_2O_3 (American Cyanimid HDS-16A)	1017	0.319	0.982	1.70	0.979

TABLE XXII

INITIAL QUINOLINE CONCENTRATION: LOADED VERSUS PREDICTED BY KINETIC MODELS

Catalyst	Run No.	Quinoline Concentration Loaded X 10^6 g mole / g_{oil}	Initial Quinoline Concentration 1st Order Model X 10^6 g mole / g_{oil}	Initial Quinoline Concentration Zero Order Model X 10^6 g mole / g_{oil}
Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A)	1020	64.65	63.57	61.69
Ni-W/Al_2O_3 (NALCO M8-550)	1023	67.59	61.10	59.80
Ni-W/Al_2O_3 (Harshaw Ni4303)	1022	68.14	66.61	65.68
Ni-W/SiO_2-Al_2O_3 (Harshaw Ni4301)	1021	67.53	62.88	62.26
Co-Mo/Al_2O_3 (American Cyanimid HDS-16A)	1017	67.74	60.83	60.62

that the pseudo first-order model fits the data better than the pseudo zero-order model; however, the zero-order model's correlation coefficients indicate that this model fits the data reasonably well. Table XXI indicates that the HDS-9A catalyst had the highest rate constants, and thus, was the most active for the hydrodenitrogenation of quinoline at these reaction conditions.

Figures 14 to 33 present graphs of the pseudo first-order kinetic analyses, pseudo zero-order kinetic analyses, rates of quinoline hydrogenation, and concentration profiles for the catalyst survey experiments. Appendix E contains detailed concentration profiles for the catalyst survey experiments.

B. Hydrodenitrogenation of Acridine

Several experiments were made to study the hydrodenitrogenation of acridine. First, a series of experiments were performed to find conditions (temperature and pressure) with which the reactivity of acridine could be studied. The range of conditions covered was 340 to 374°C and 500 to 2000 psig. These experiments were also used to identify reaction products using mass spectroscopy. Another set of experi-

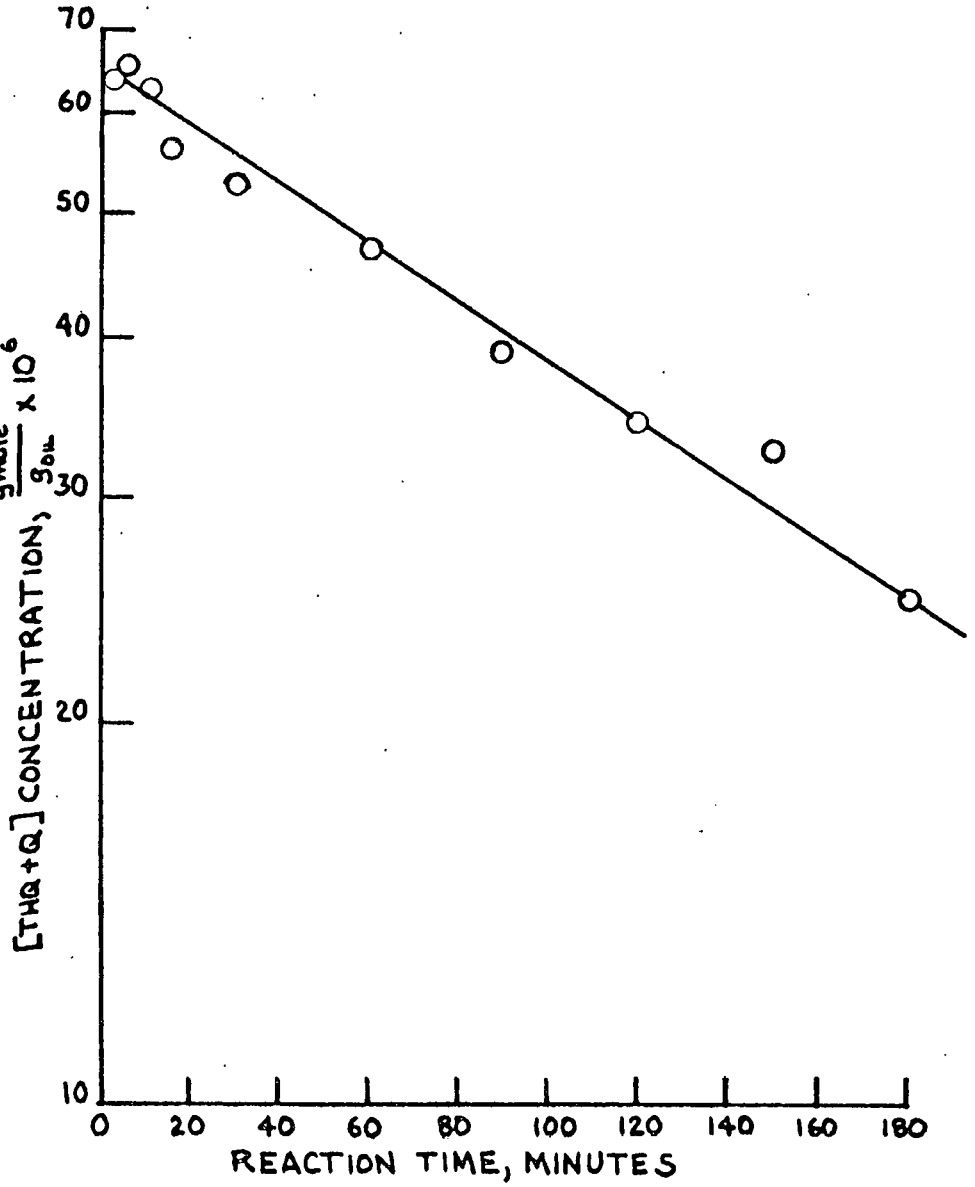


Figure 14. Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline for Run 1020: 342°C and 500 psig, Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

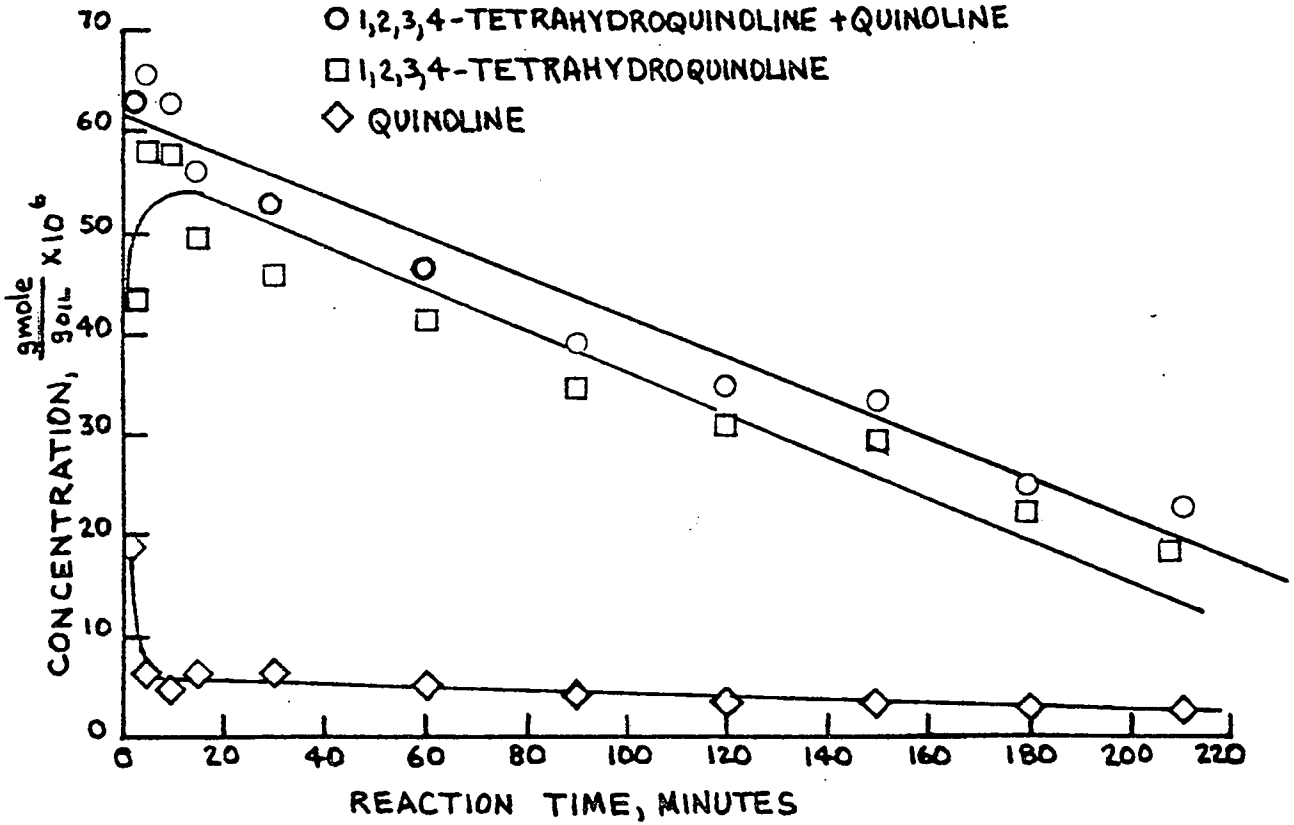


Figure 15. Pseudo Zero-Order Kinetic Analysis for the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline and Concentration Profiles for Quinoline and for 1,2,3,4-tetrahydroquinoline: Run 1020; 342°C and 500 psig, Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

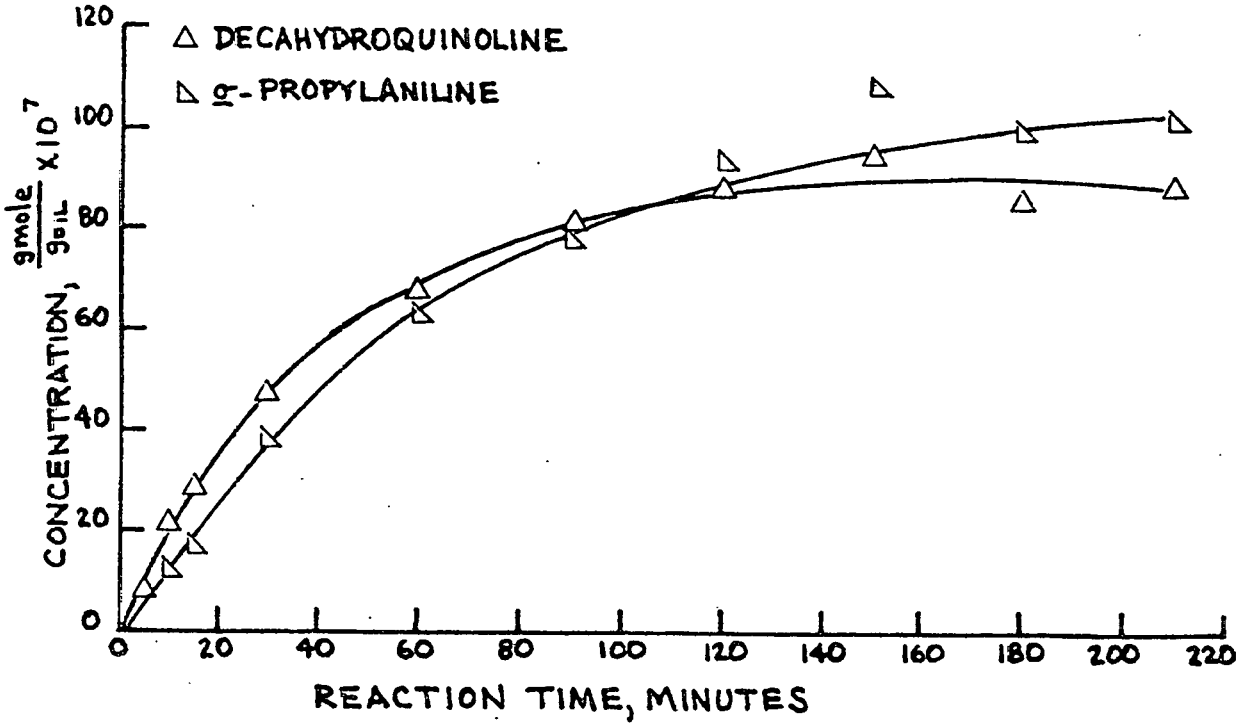


Figure 16. Concentration Profiles for Decahydroquinoline and for o-propylaniline: 342°C and 500 psig (Run 1020); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

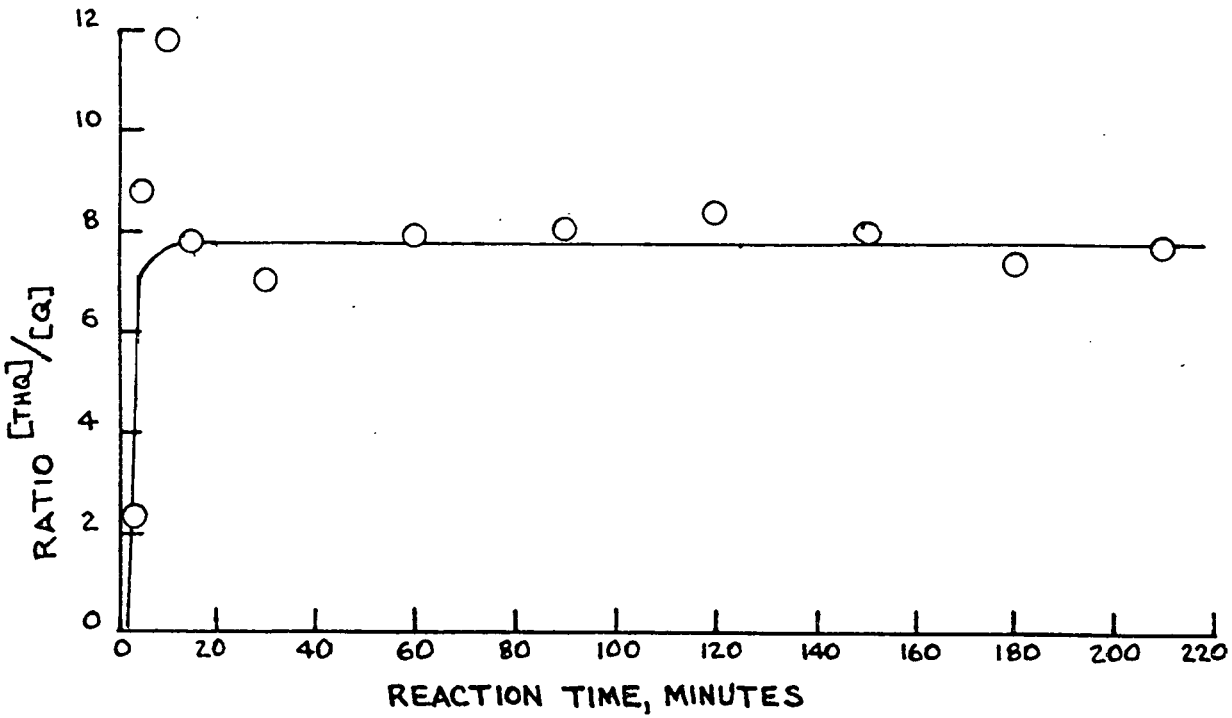


Figure 17. Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1020); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

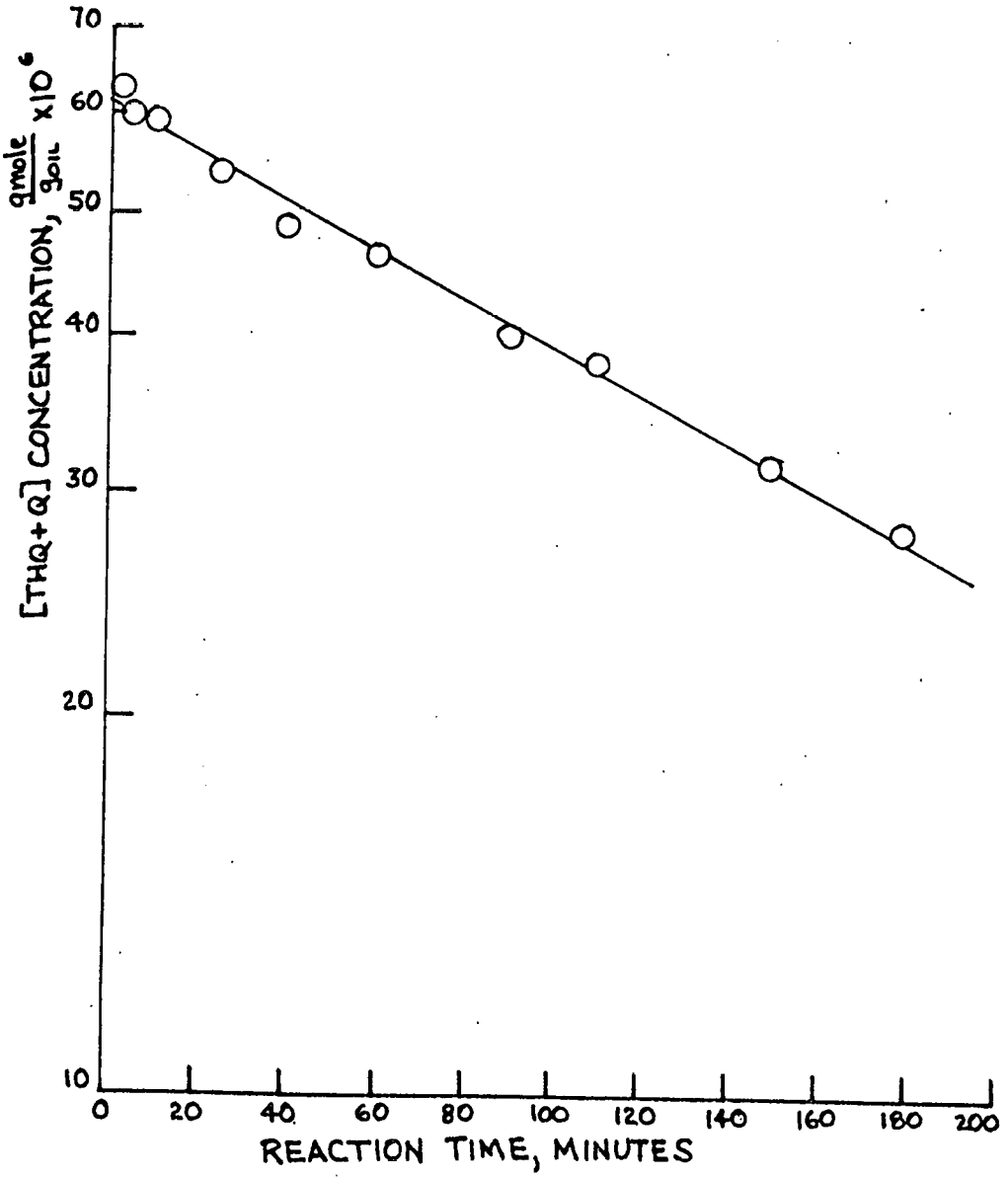


Figure 18. Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1023); Ni-W/Al_2O_3 (NALCO NT-550) Catalyst.

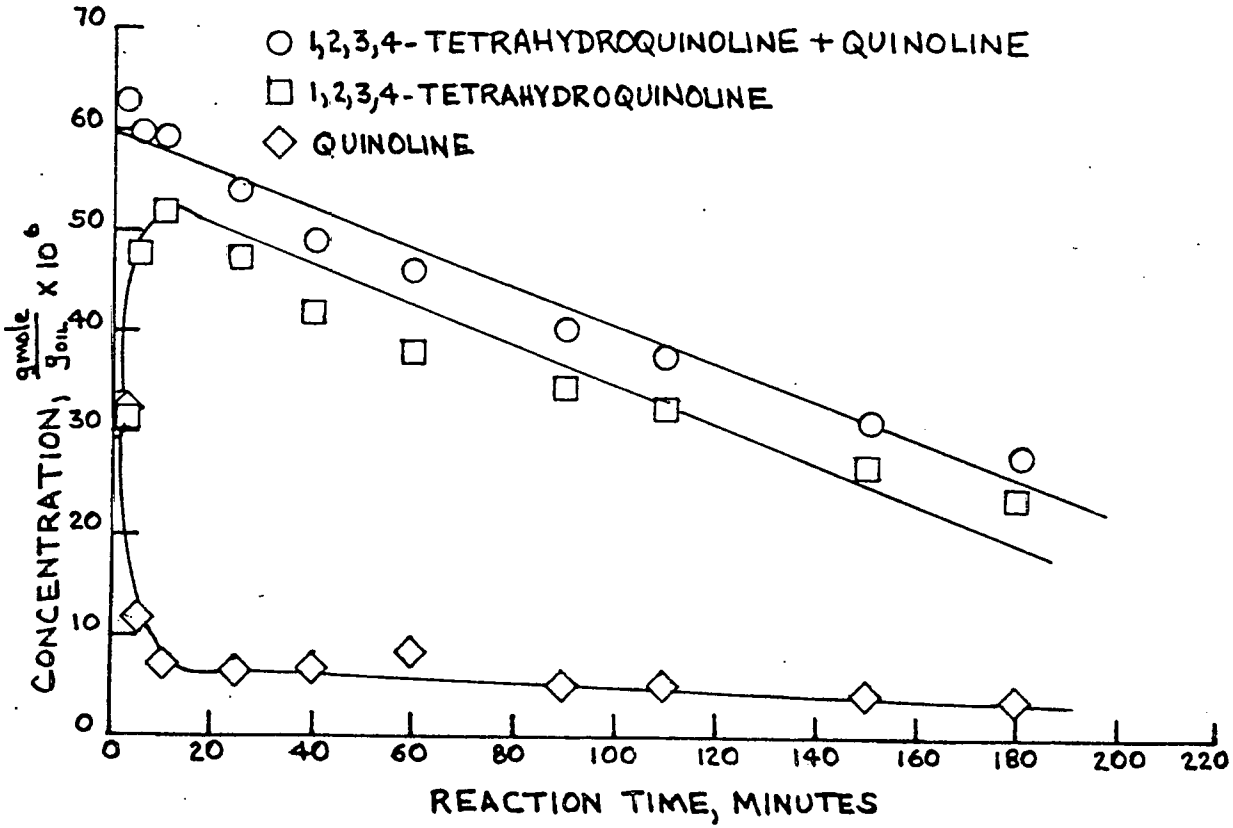


Figure 19. Pseudo Zero-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline and Concentration Profiles for Quinoline and for 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1023); Ni-W/Al_2O_3 (NALCO NT-550) Catalyst.

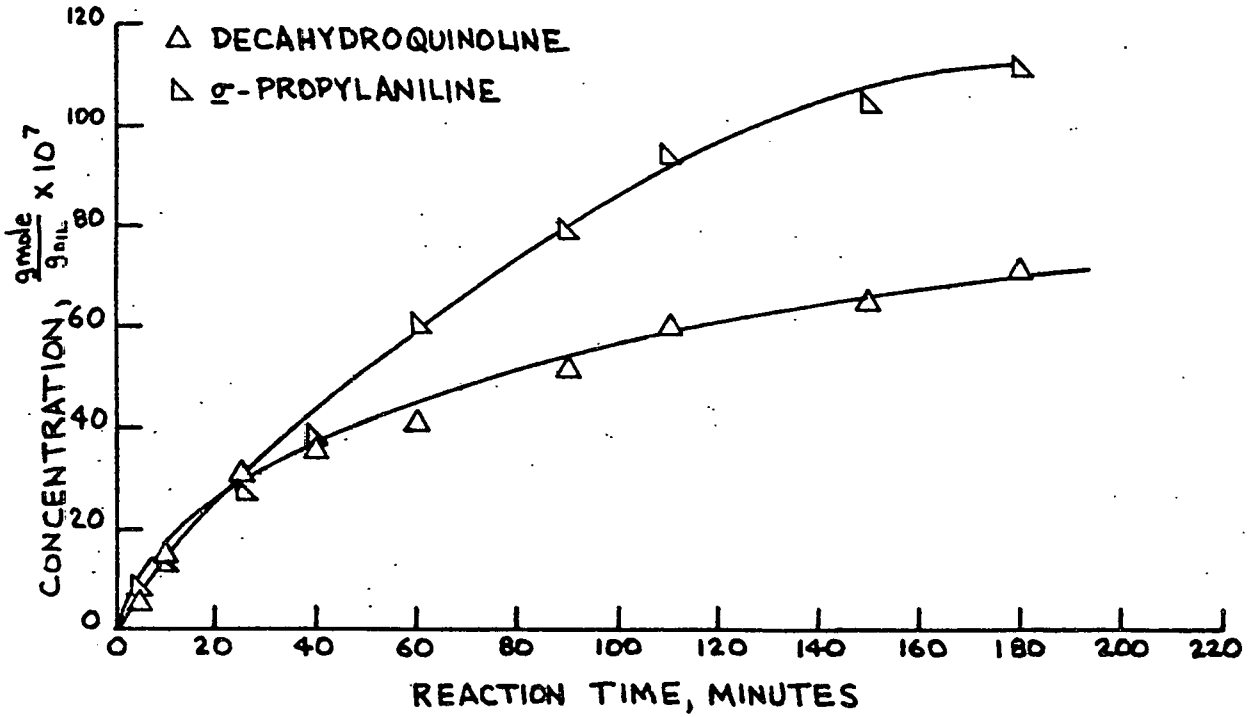


Figure 20. Concentration Profiles for Decahydroquinoline and for o-propylaniline: 342°C and 500 psig (Run 1023); Ni-W/Al_2O_3 (NALCO NT-550) Catalyst.

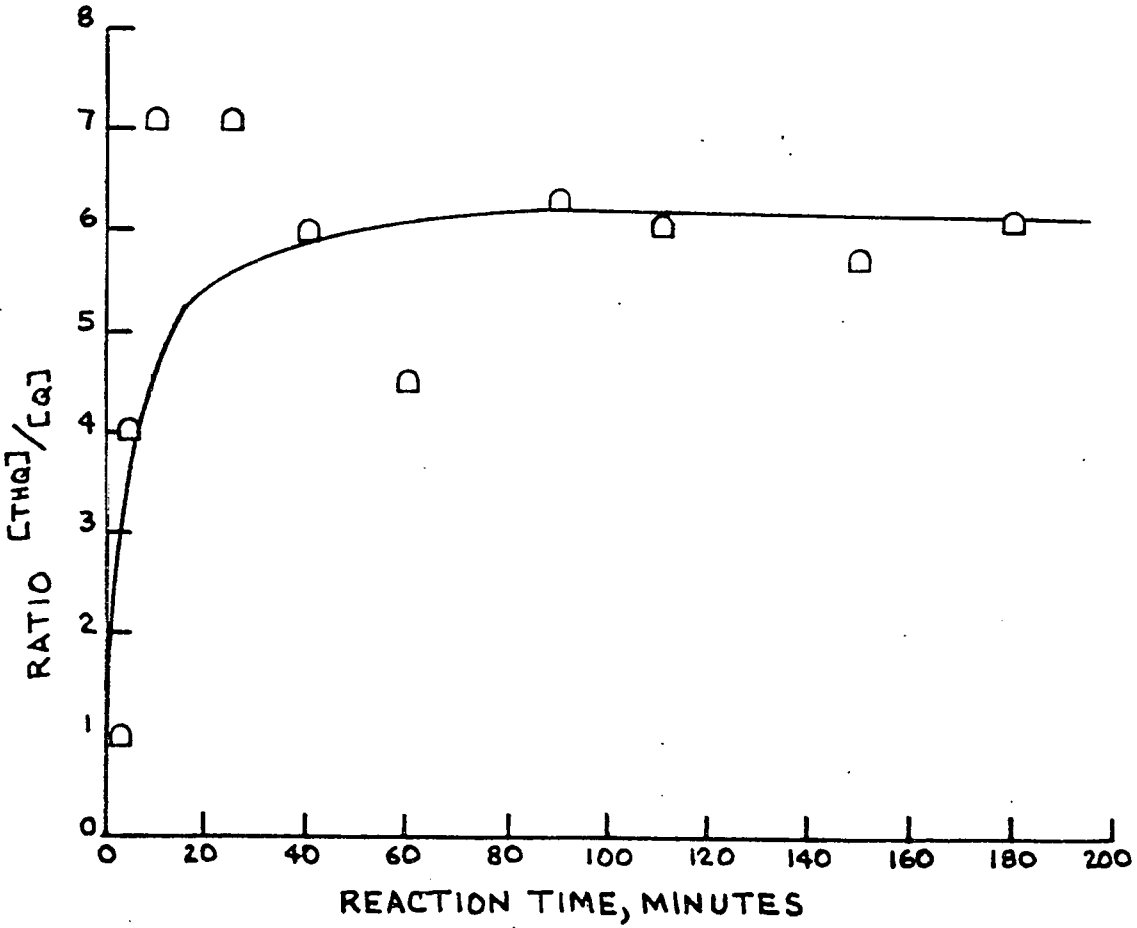


Figure 21. Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1023); Ni-W/Al_2O_3 (NALCO NT-550) Catalyst.

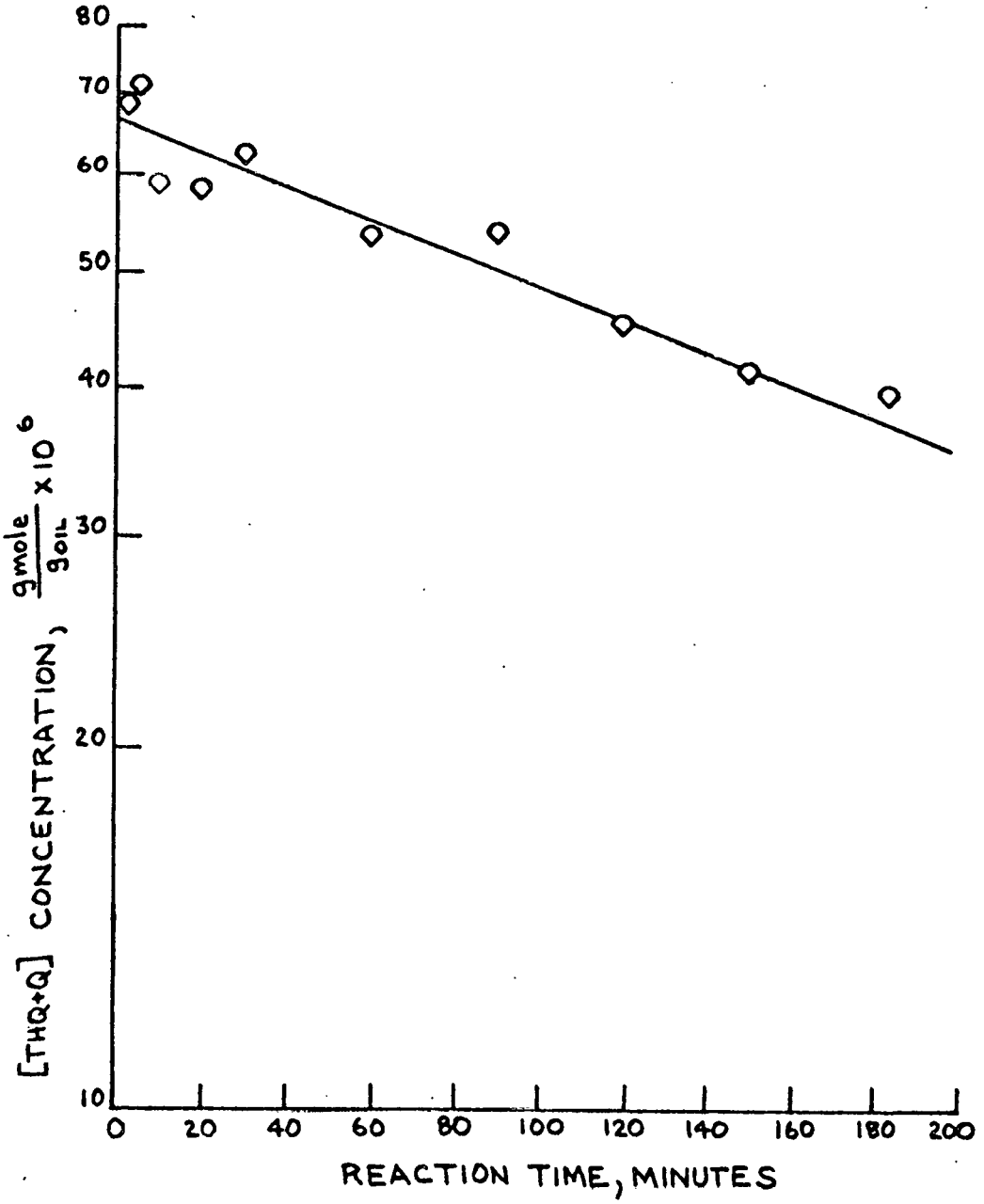


Figure 22. Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2, 3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1022); Ni-W/Al_2O_3 (Harshaw Ni4303) Catalyst.

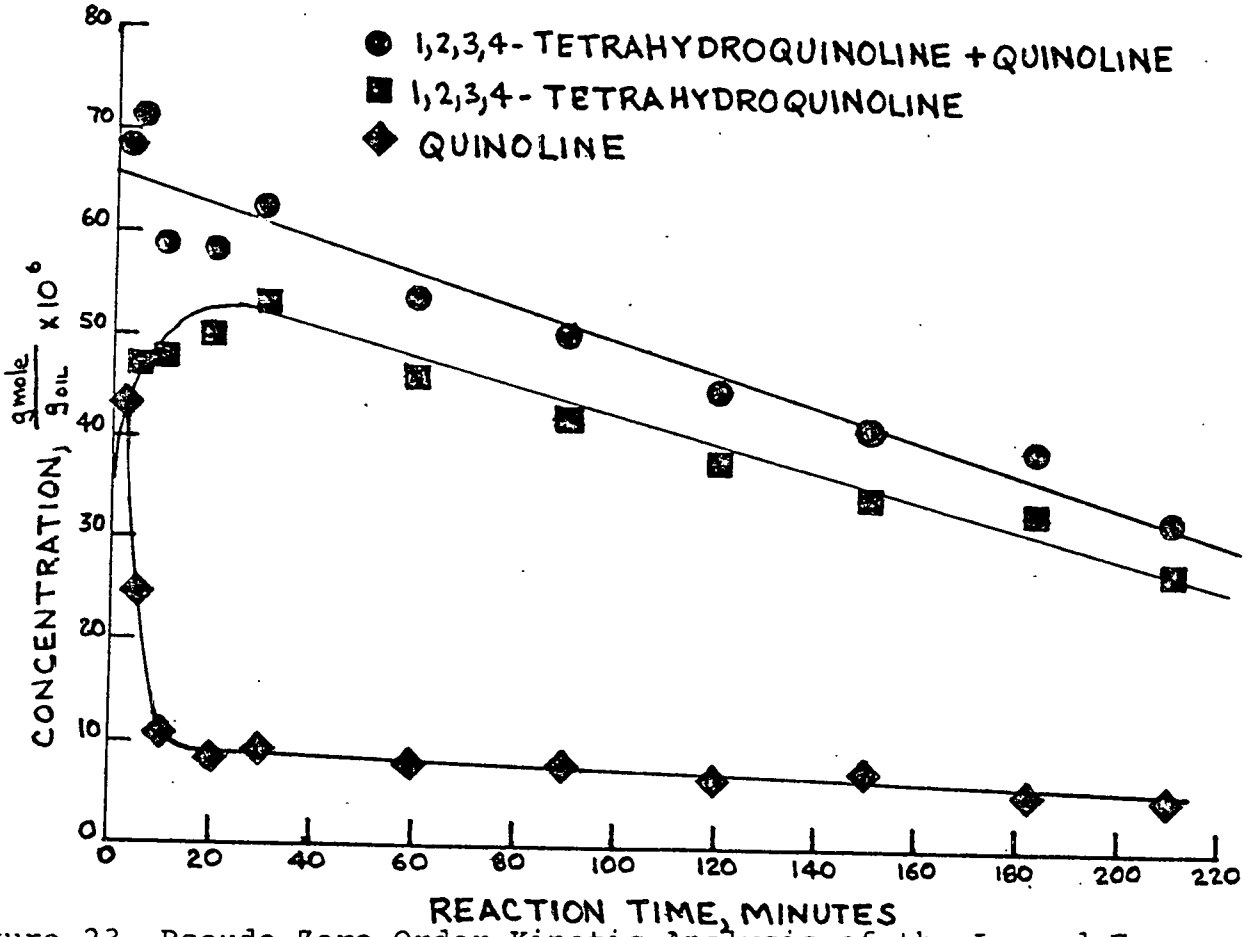


Figure 23. Pseudo Zero-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline and Concentration Profiles for Quinoline and for 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1022); Ni-W/Al_2O_3 (Harshaw Ni4303) catalyst.

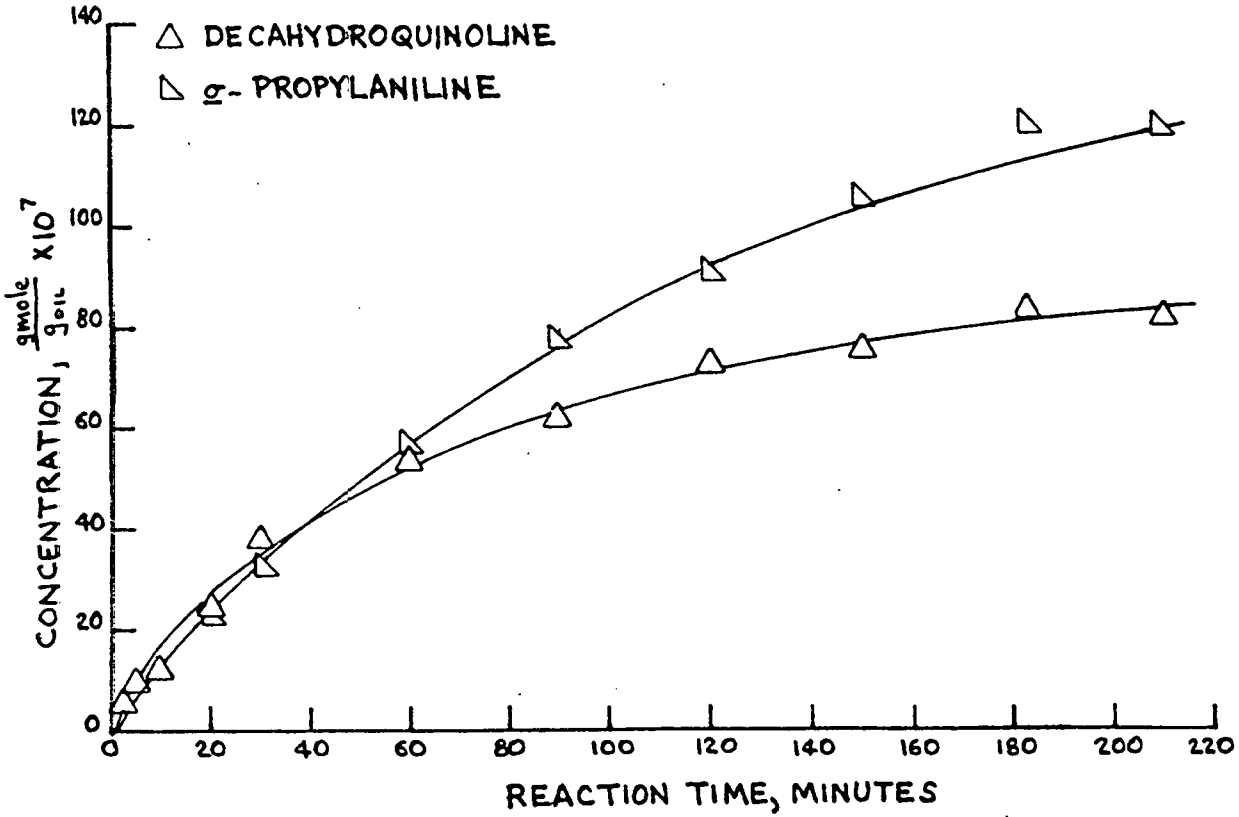


Figure 24. Concentration Profiles for Decahydroquinoline and for o-propylaniline: 342°C and 500 psig (Run 1022); Ni-W/Al_2O_3 (Harshaw Ni4303) Catalyst.

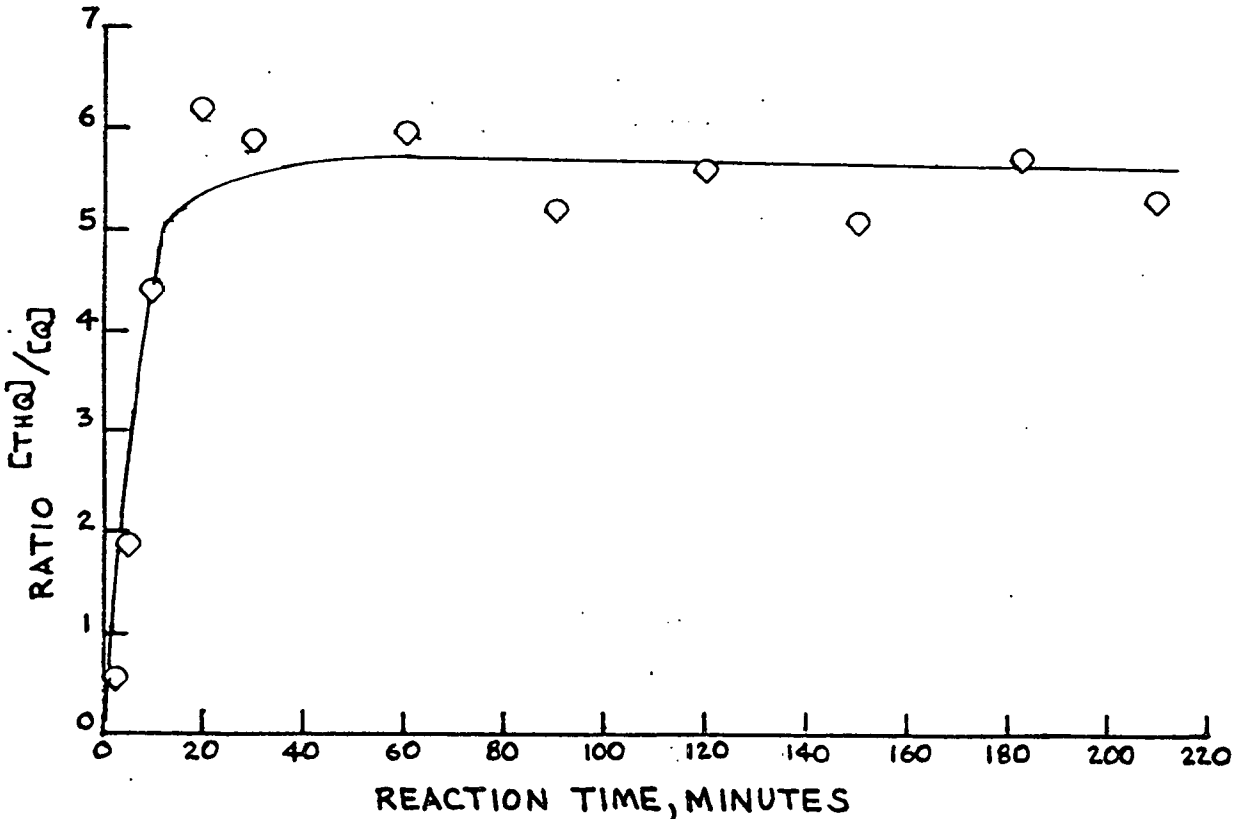


Figure 25. Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1022); Ni-W/Al_2O_3 (Harshaw Ni4303) Catalyst.

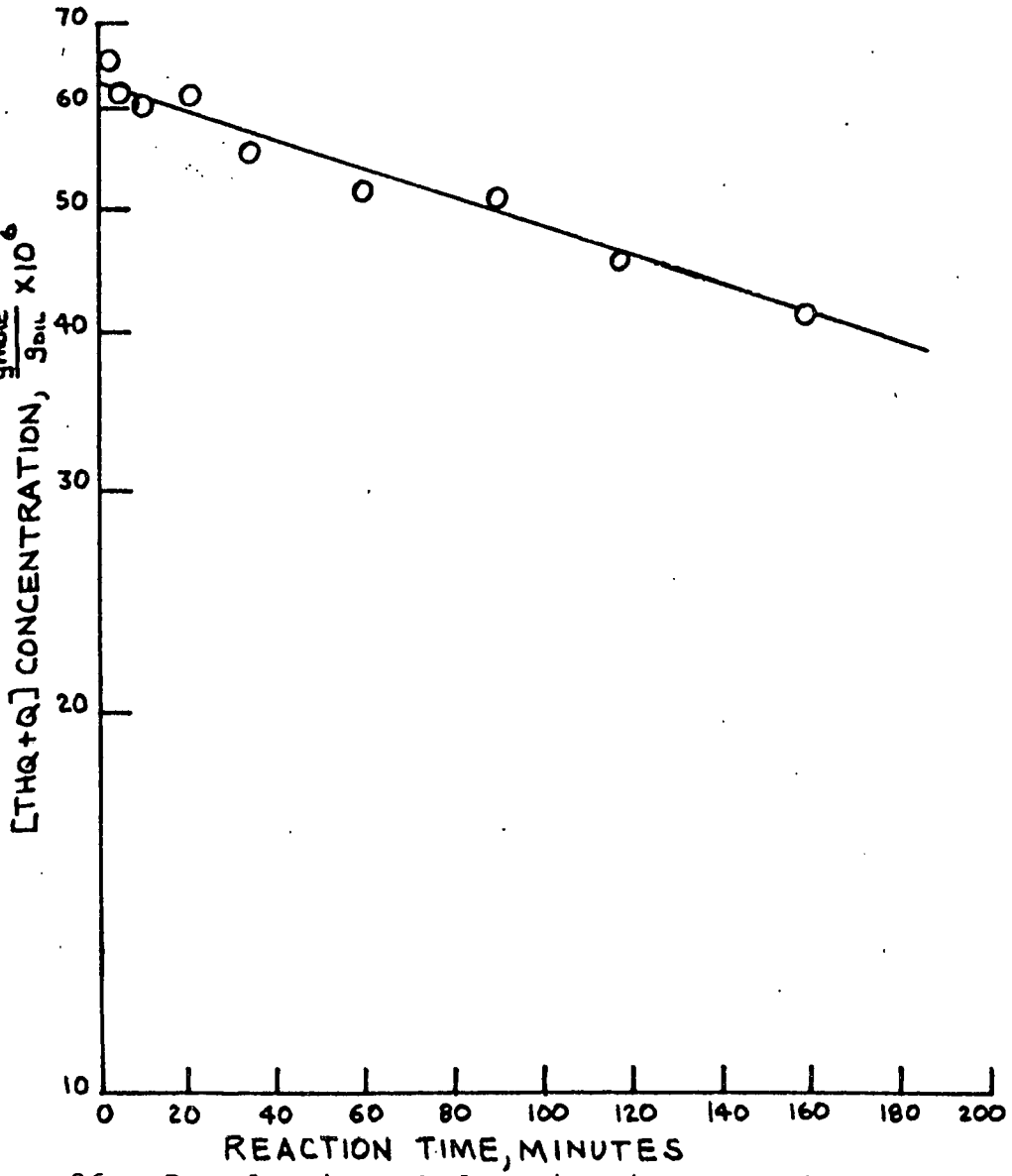


Figure 26. Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1021); Ni-W/Al_2O_3-SiO_2 (Harshaw Ni4301) Catalyst.

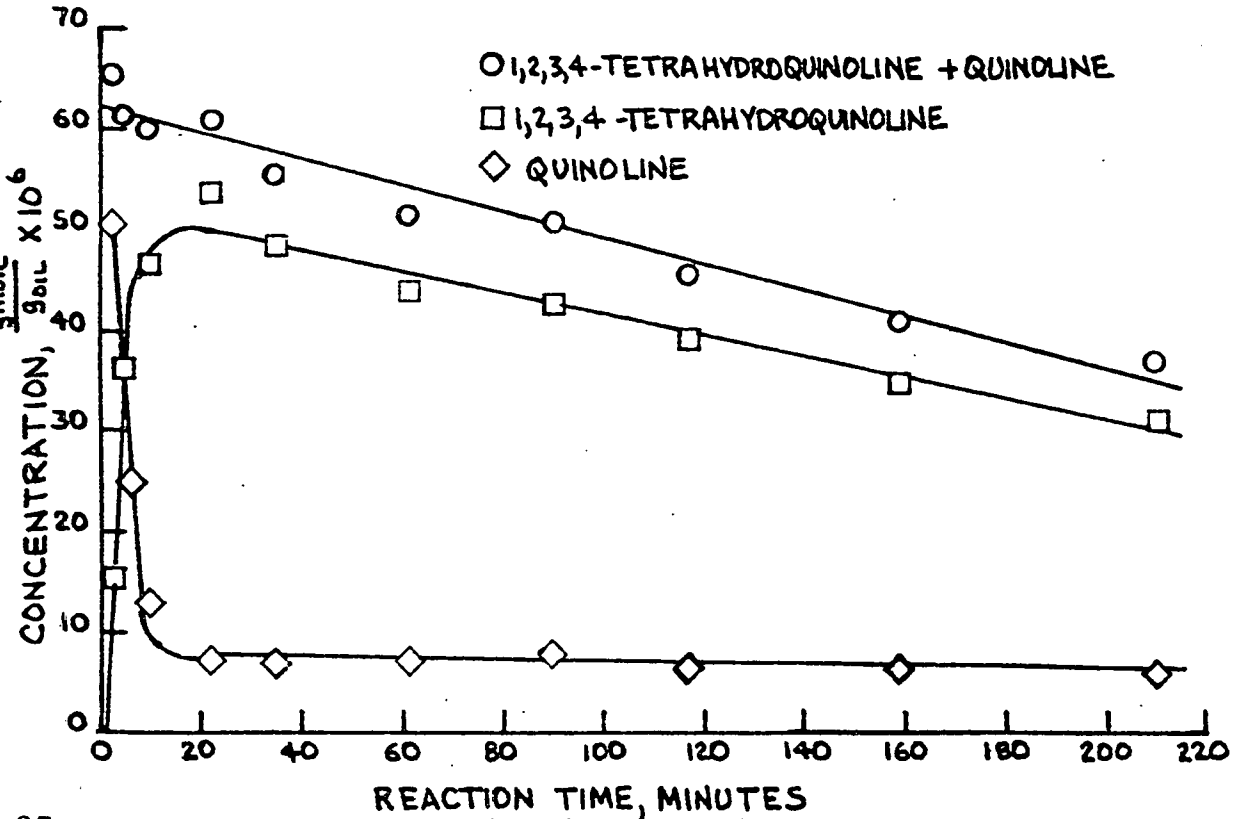


Figure 27. Pseudo Zero-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline and Concentration Profiles for Quinoline and for 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1021); Ni-W/Al_2O_3-SiO_2 (Harshaw Ni4301) Catalyst.

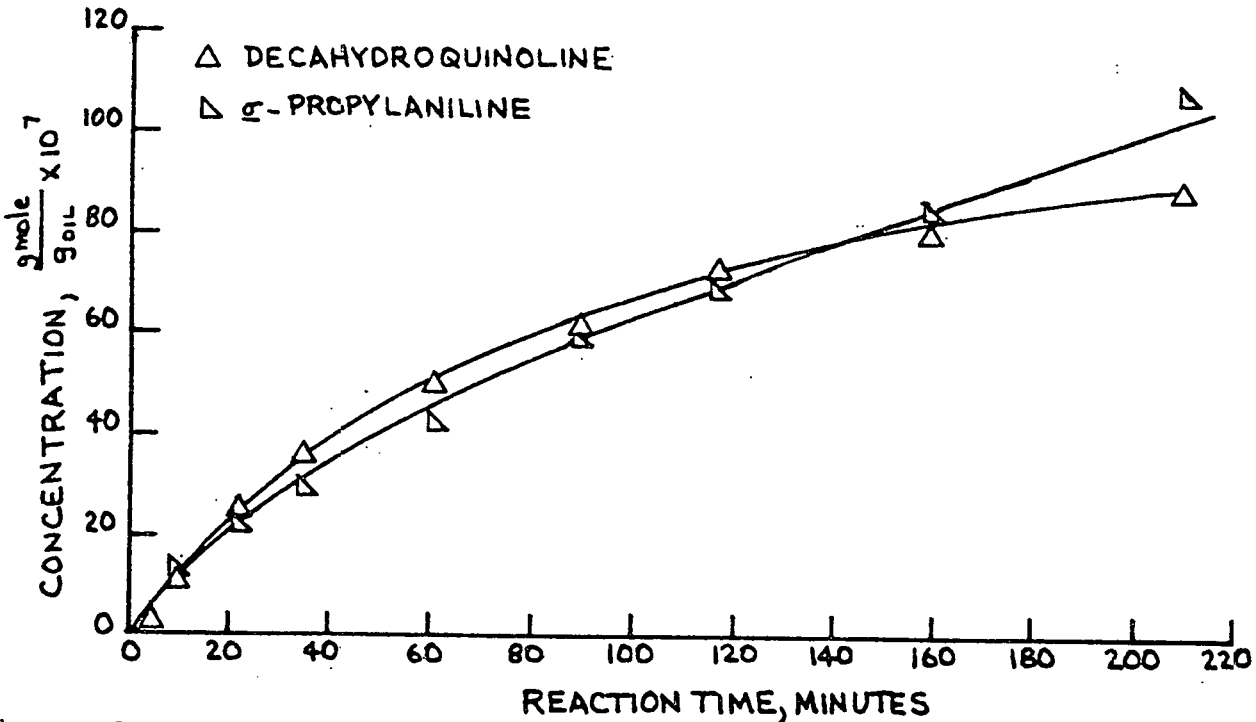


Figure 28. Concentration Profiles for Decahydroquinoline and for o-propylaniline: 342°C and 500 psig (Run 1021); Ni-W/Al_2O_3-SiO_2 (Harshaw Ni4301) Catalyst.

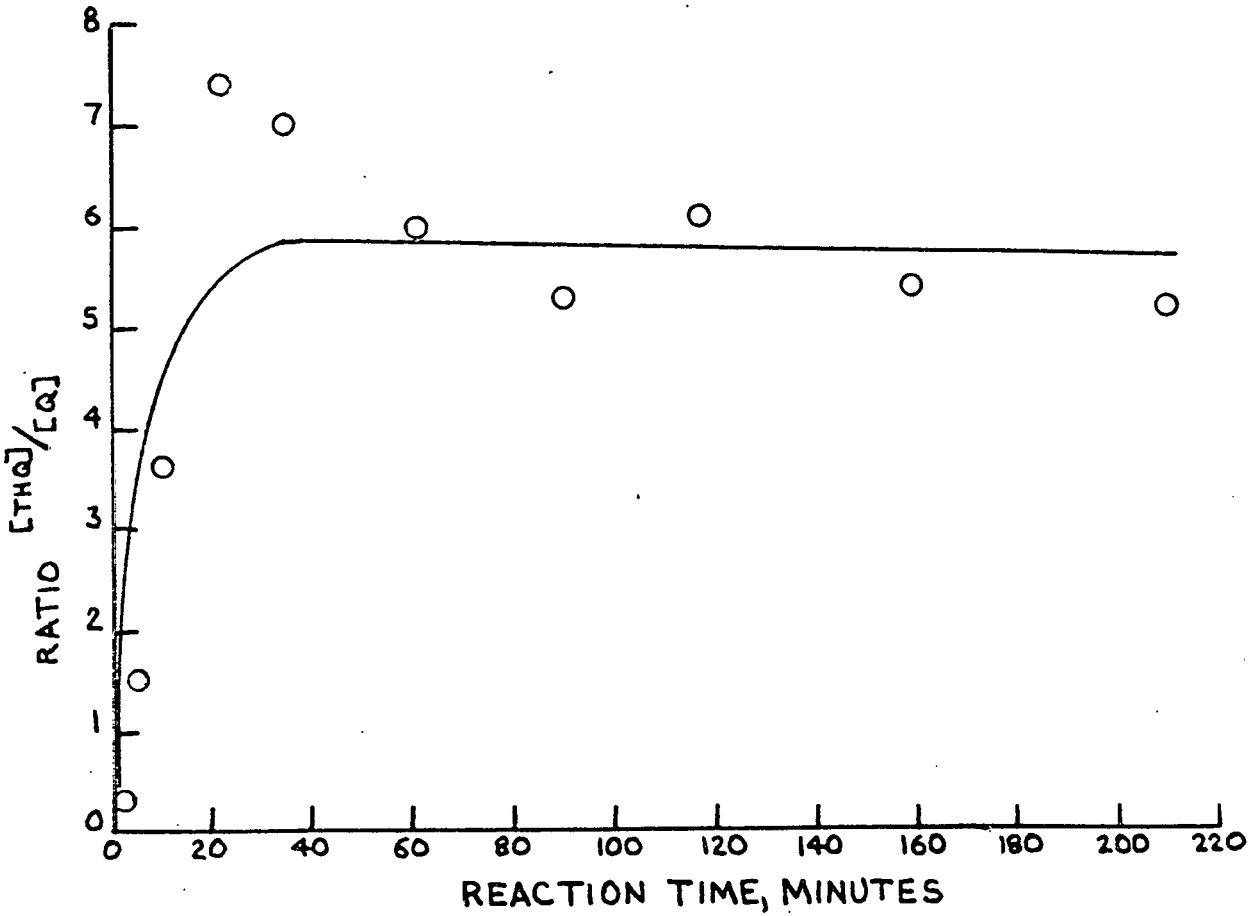


Figure 29. Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1021); Ni-W/Al_2O_3-SiO_2 (Harshaw Ni4301) Catalyst.

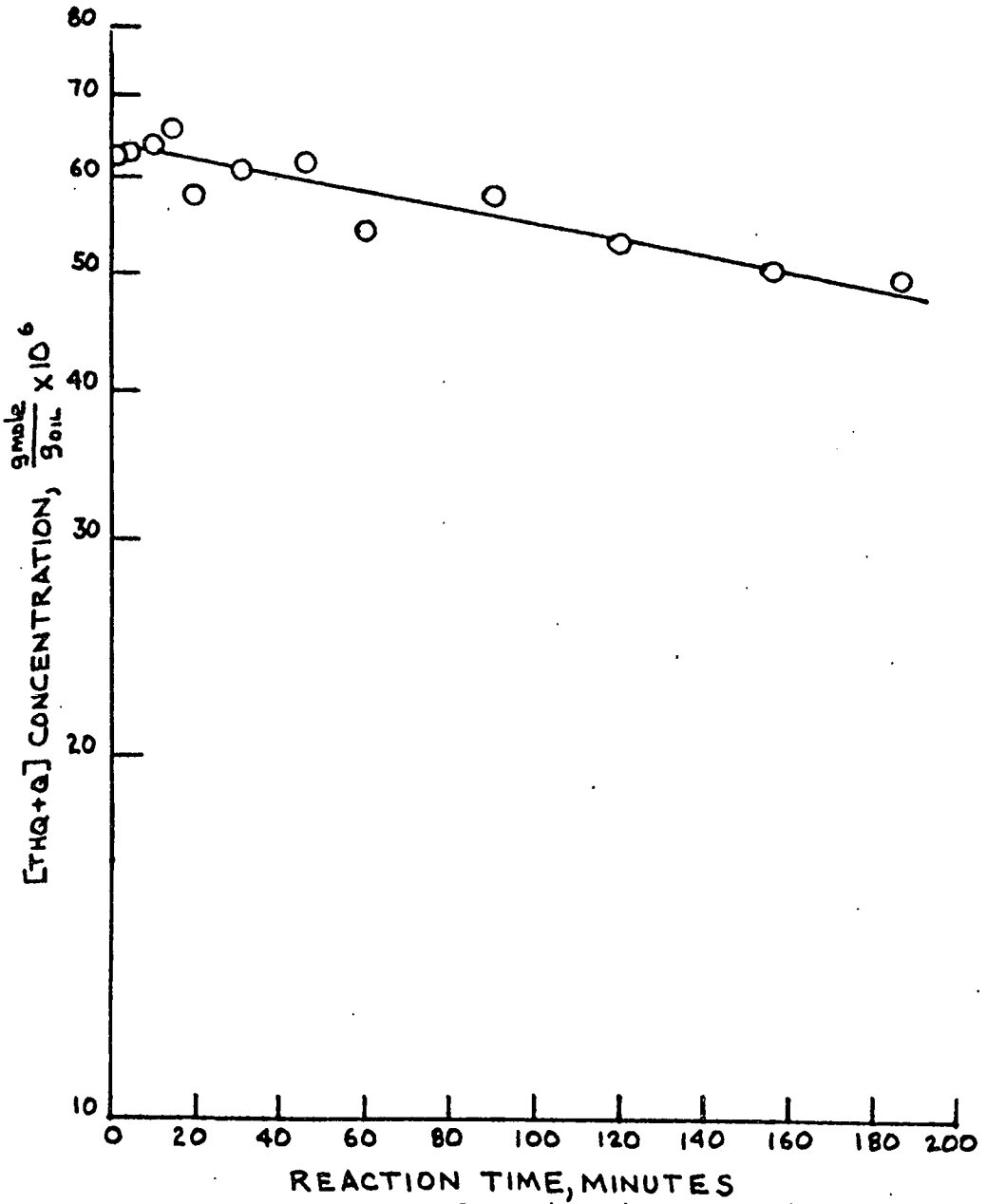


Figure 30. Pseudo First-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1017); Co-Mo/Al_2O_3 (American Cyanimid HDS-16A) Catalyst.

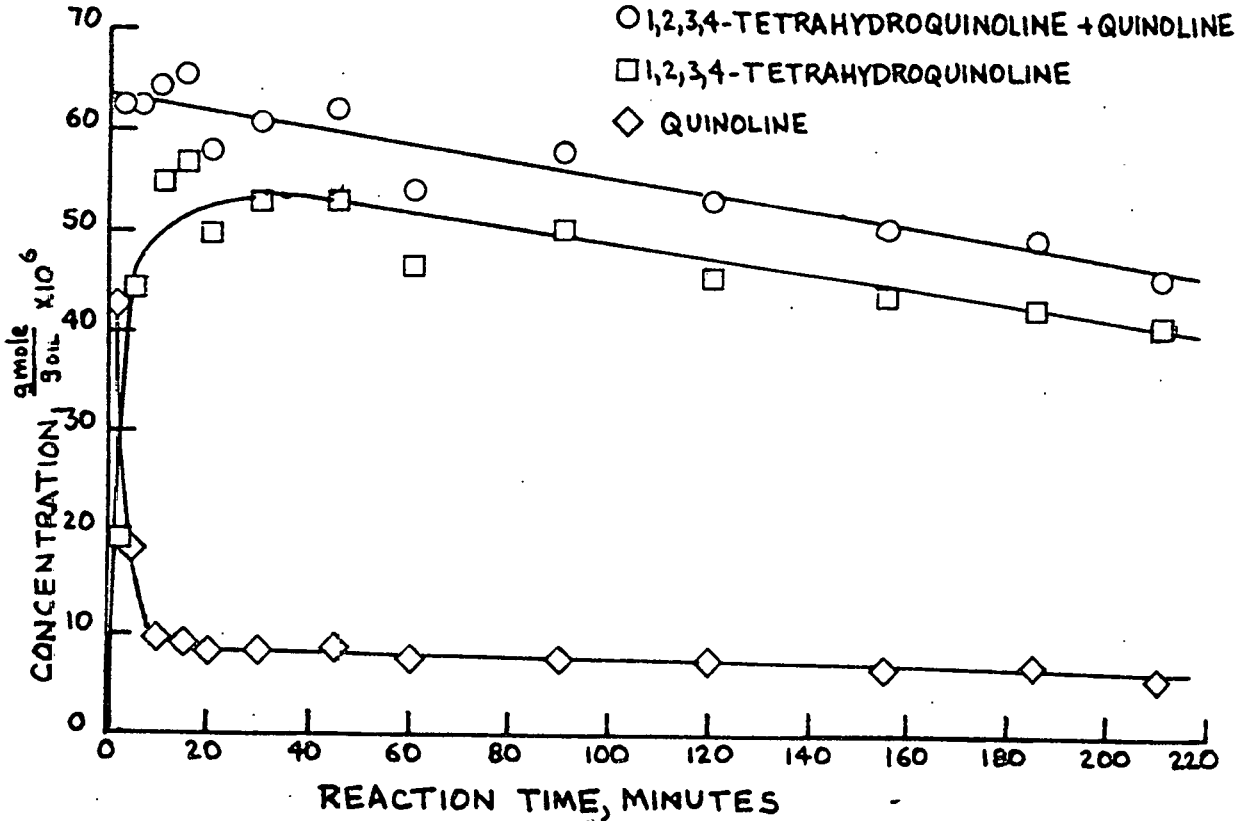


Figure 31. Pseudo Zero-Order Kinetic Analysis of the Lumped Group of Quinoline Plus 1,2,3,4-tetrahydroquinoline and Concentration Profiles for Quinoline and for 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1017); Co-Mo/Al_2O_3 (American Cyanimid HDS-16A) Catalyst.

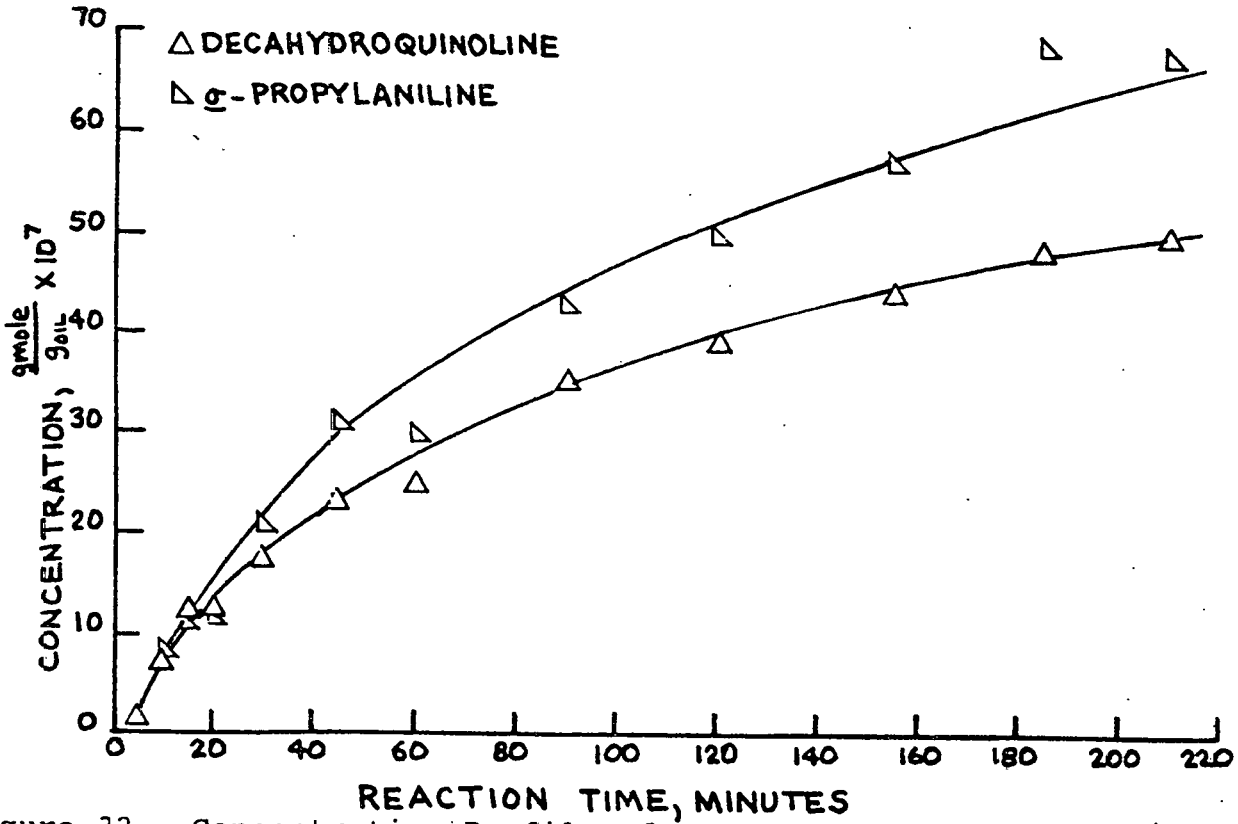


Figure 32. Concentration Profiles for Decahydroquinoline and for o-propylaniline: 342°C and 500 psig (Run 1017); Co-Mo/Al_2O_3 (American Cyanimid HDS-16A) Catalyst.

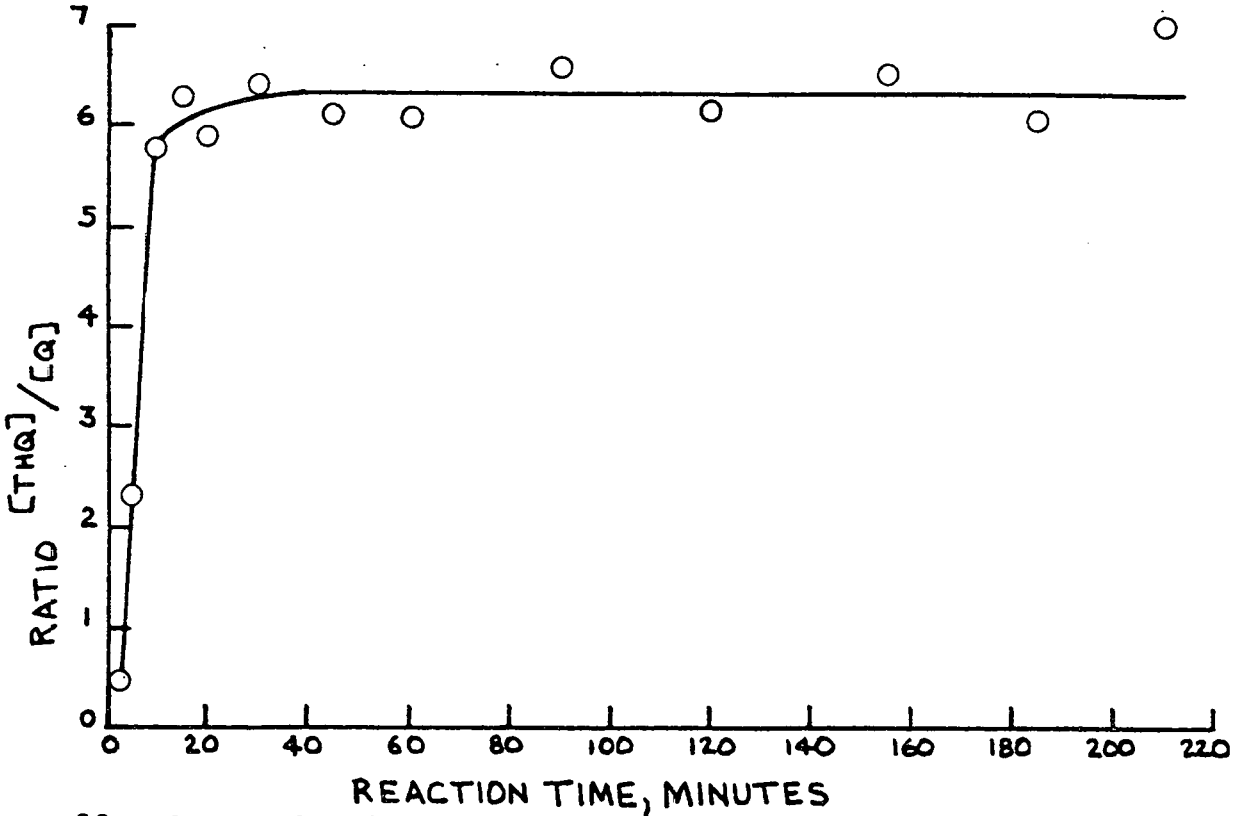


Figure 33. Rate of Quinoline Hydrogenation to 1,2,3,4-tetrahydroquinoline: 342°C and 500 psig (Run 1017); Co-Mo/Al_2O_3 (American Cyanimid HDS-16A) Catalyst.

ments was performed to evaluate the presence of any significant mass transfer effects. An autoclave reactor stirring speed range of 500 to 1250 rpm was scanned for possible significant gas-liquid mass transfer resistances. A range of catalyst particle sizes of 90 μm to 275 μm was scanned for possible significant intraparticle mass transfer effects. All the experiments concerning the evaluation of mass transfer effects were performed at 342°C and 500 psig. Finally, a blank (no catalyst) reactor experiment was performed over a temperature range of 340 to 380°C and a pressure of 500 psig to analyze the intrinsic reactivity of acridine.

The search for a suitable chromatographic column with which to analyze the nitrogen-containing reaction products of acridine took place during the same time period that the reaction experiments were performed. A column that could resolve all the reaction products was never found. Apiezon L (2% KOH) was finally chosen so that estimates of some of the product distributions and an estimate of total nitrogen removal could be obtained from some of the experiments. Further discussion of these analytical problems

is presented in Appendix F. Since the column search took an excessively long time (about 6 months) and was not totally successful, analysis of all the acridine experiments discussed in the preceeding paragraph was not possible. Analyses of only 2 experiments in the first series of experiments (reactivity conditions search) were obtained and reported in this thesis.

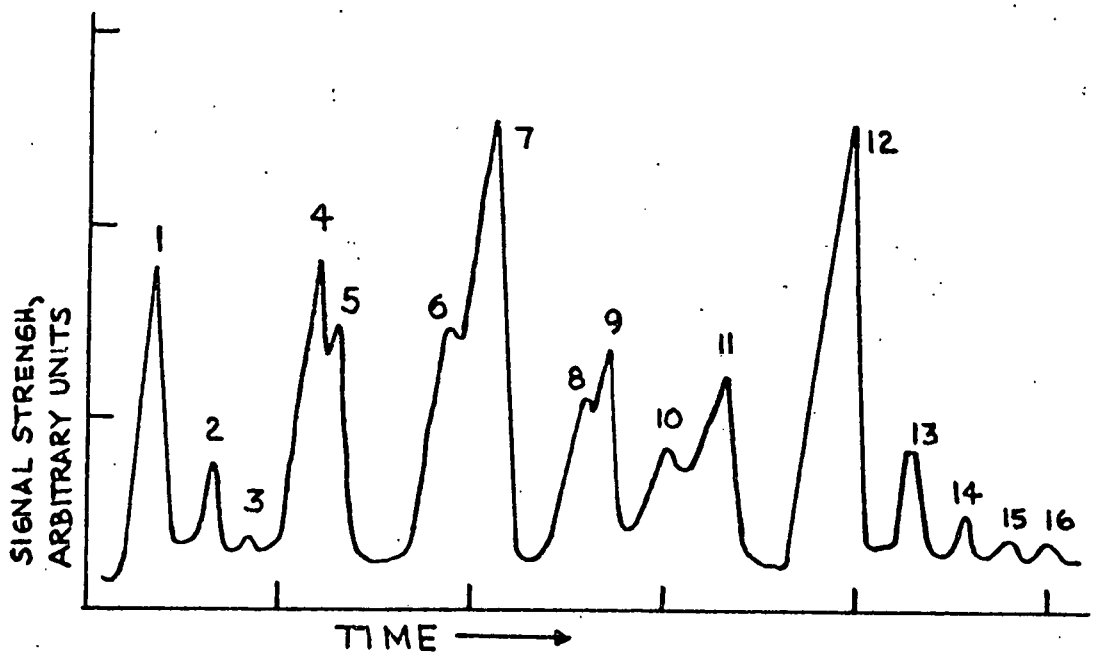
Reaction conditions for the two experiments for which analysis of reaction products was secured are shown in Table XXIII. The nitrogen-containing reaction products were extracted from the oil (procedure in Appendix G) and were analyzed on the gas chromatography-mass spectrometer system. There were no products in the experiment at the less severe conditions (Run 1042) that were not present in the experiment at the more severe conditions (Run 1050). Therefore, further presentation and discussion of the identification of reaction products concerns Run 1050.

A total of 16 nitrogen-containing reaction products including acridine were present in the extract. A pseudo-chromatogram of these products is shown in Figure 34. This figure is a condensation of

TABLE XXIII

REACTION CONDITIONS FOR THE ANALYZED ACRIDINE EXPERIMENTS

Run Number	1042	1050
Temperature, °C	342	353
Pressure, psig	500	2000
Reactant	0.5wt% acridine in n-hexadecane	White oil
Catalyst	[2g/500 cc oil]	
Catalyst Particle Size	[140-200 mesh (90 μm)]	
Catalyst Presulfided	Yes	
CS_2 added to medium	0.05 wt%	



PEAK	MOLECULAR WEIGHT	STRUCTURE
1	152	
2	153	
3	153	
4	174	
5	153	
6	193	
7	193	PER-HYDROACRIDINE
8	187	
9	193	
10	187	
11	189	o-(METHYLENECYCLOHEXANE)ANILINE
12	187	SYM-OCTAHYDROACRIDINE
13	187	1,2,3,4,9,10,13,14-OCTAHYDROACRIDINE
14	183	1,2,3,4-TETRAHYDROACRIDINE
15	179	ACRIDINE
16	201	

Figure 34. Chromatogram of the Extracted Nitrogen-containing Reaction Products for the Acridine Experiment Run at 353°C and 2000 psig (Run 1052); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

several chromatograms run on a 10 foot Apiezon L (2% KOH) chromatographic column at various temperatures between 120 and 200°C. The figure is representative of the relative concentrations of the compounds present and of the degree of resolution obtained. As shown in Figure 34, six compounds were identified as to molecular structure and the remaining compounds were assigned a molecular weight. The molecular structure was assigned based on mass spectral fragmentation patterns given in Appendix I. Mass spectra for the six identified compounds are shown in Figures 35 through 40. More details about the mass spectroscopic analysis and the problems incurred are presented in Appendix H. Detailed mass spectra and mass spectral fragmentation patterns are presented in Appendix I.

A chromatogram of a reactor sample for Run 1050 (353°C and 2000 psig) is shown in Figure 41.* The numbers assigned to the peaks refer to the compound assignments in Figure 34. Figures 42 and 43 present compound distributions for Run 1042 (340°C, 500 psig) and run 1050 (353°C, 2000 psig), respectively. The total nitrogen curve in Figure 42 indicates that essen-

* Chromatographic conditions are given in Table XV in Chapter II.

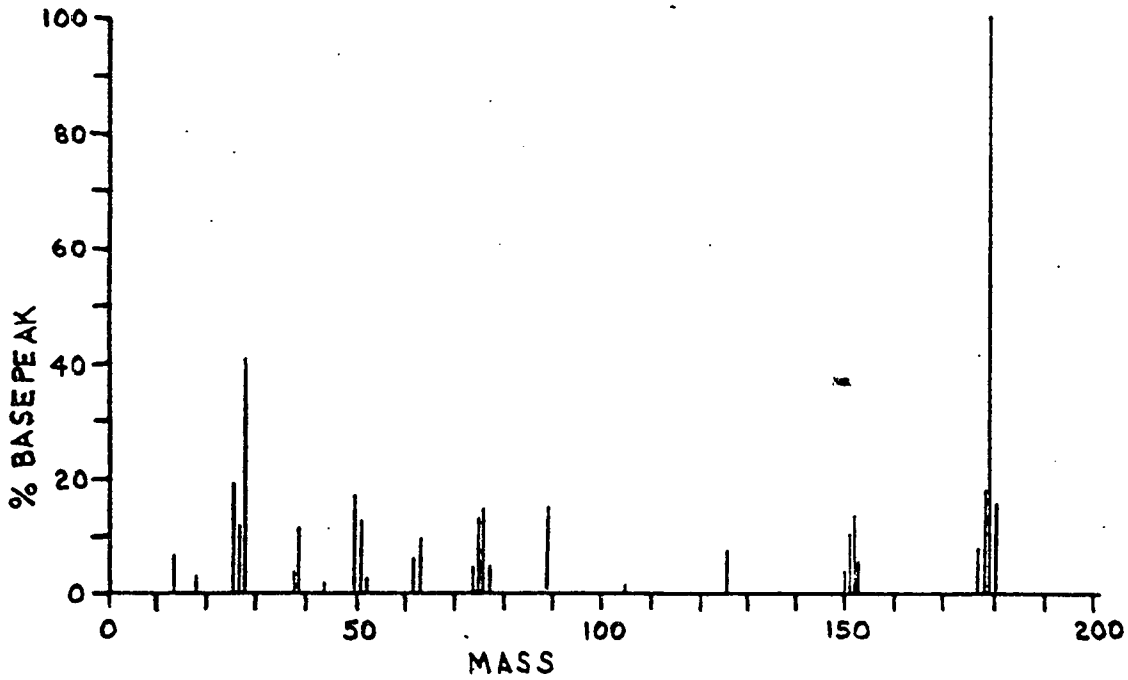


Figure 35. Mass Spectrum for Acridine.

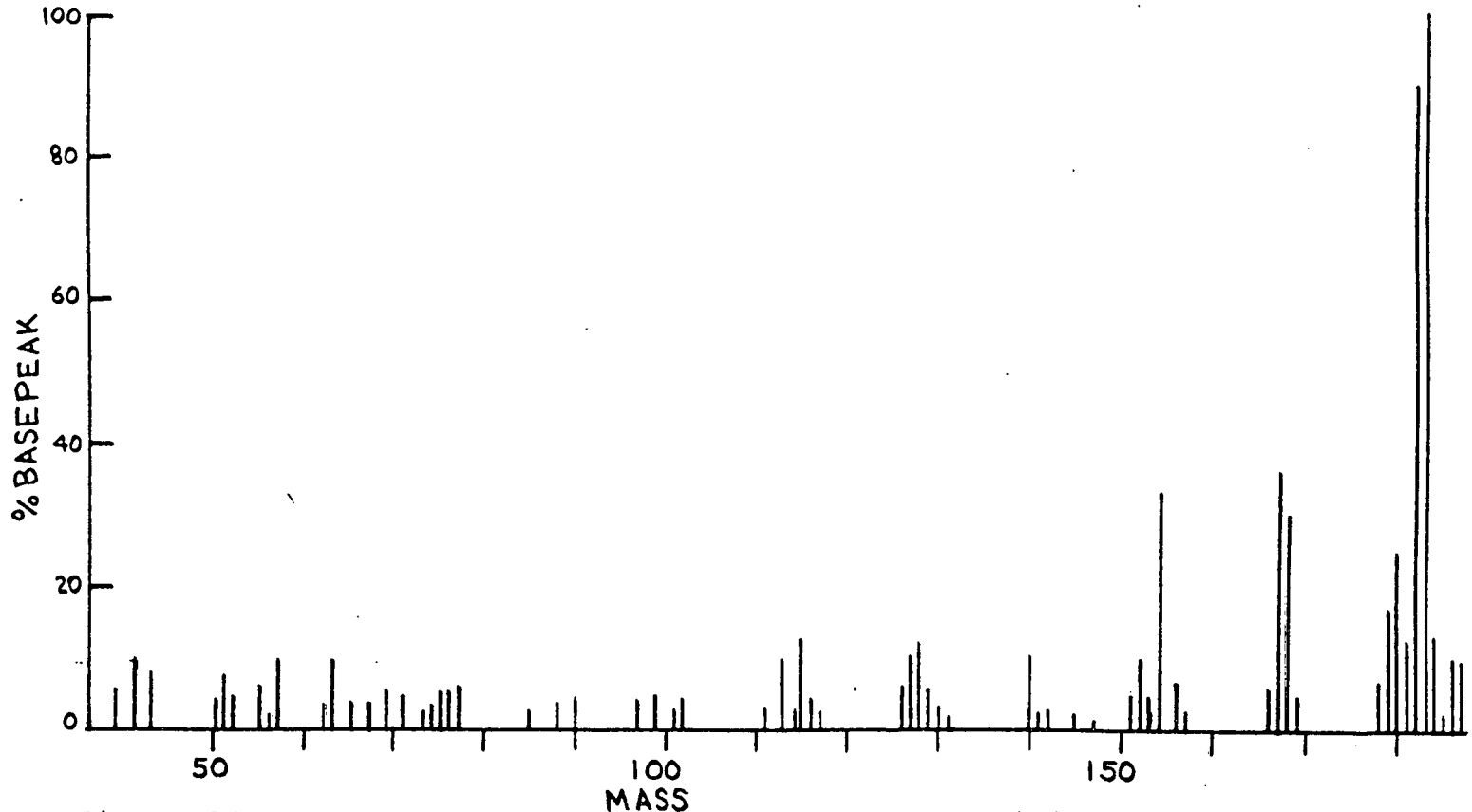


Figure 36. Mass Spectrum for 1,2,3,4-tetrahydroacridine.

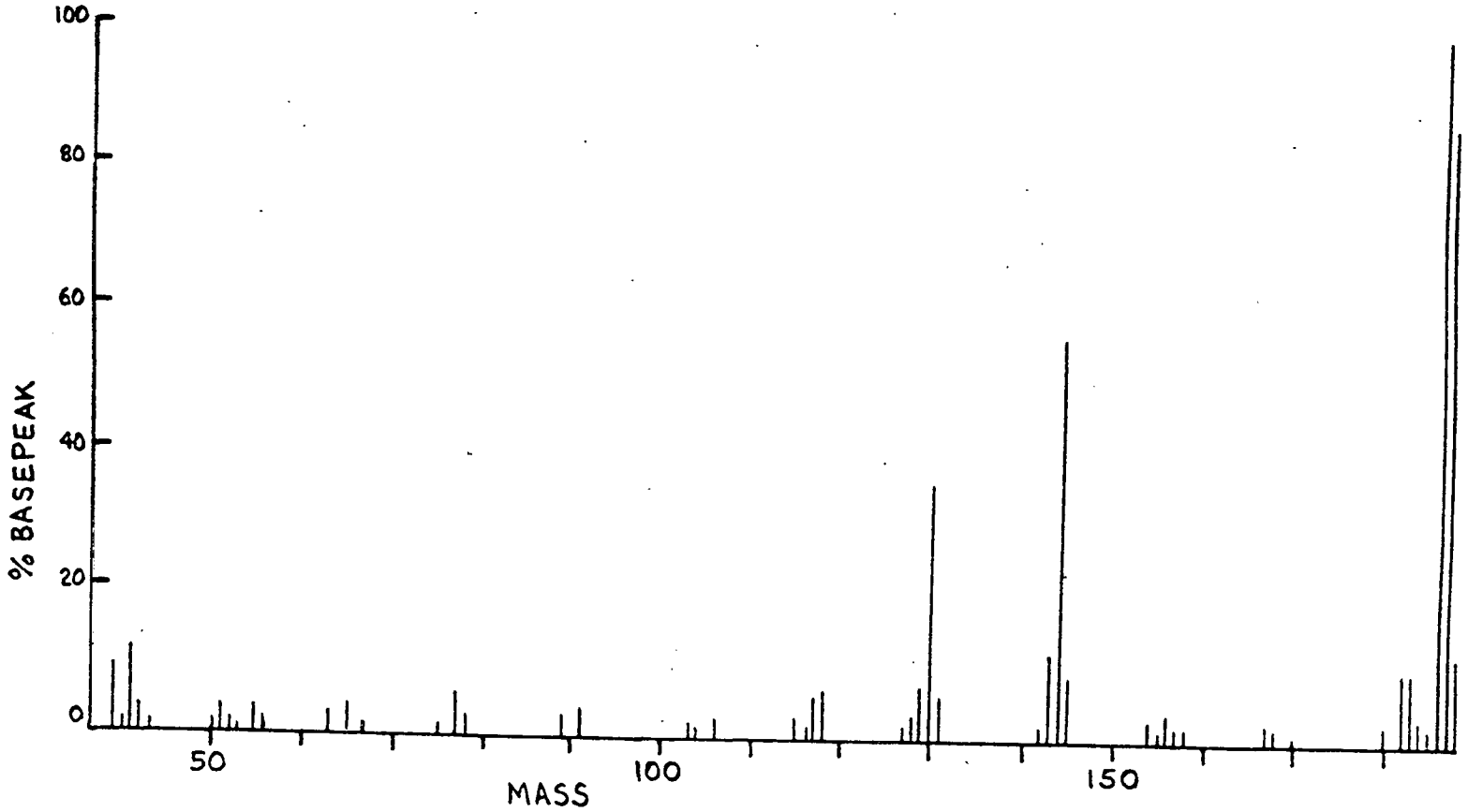


Figure 37. Mass Spectrum for 1,2,3,4,9,10,13,14-octahydroacridine.

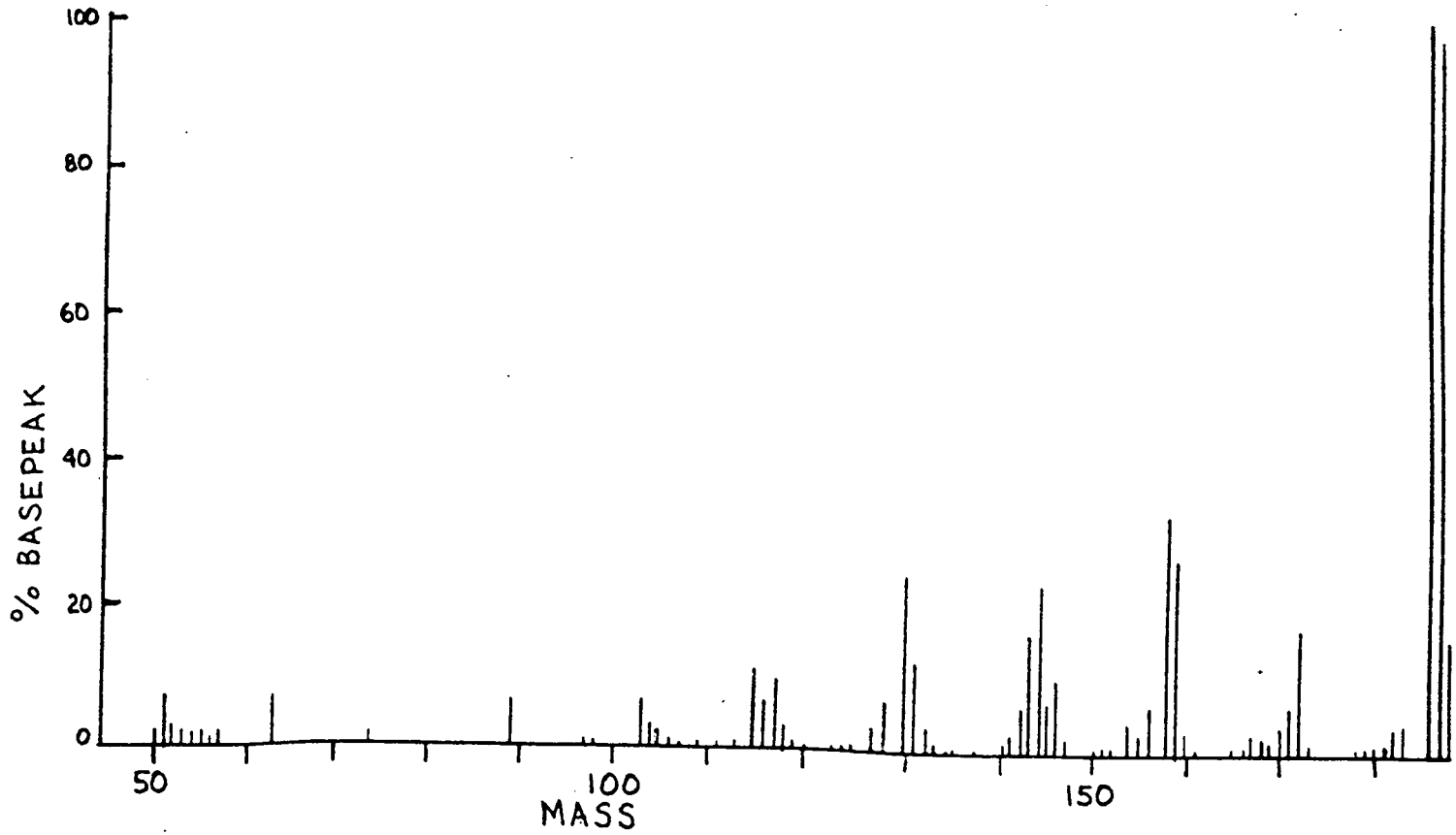


Figure 38. Mass Spectrum for sym-octahydroacridine.

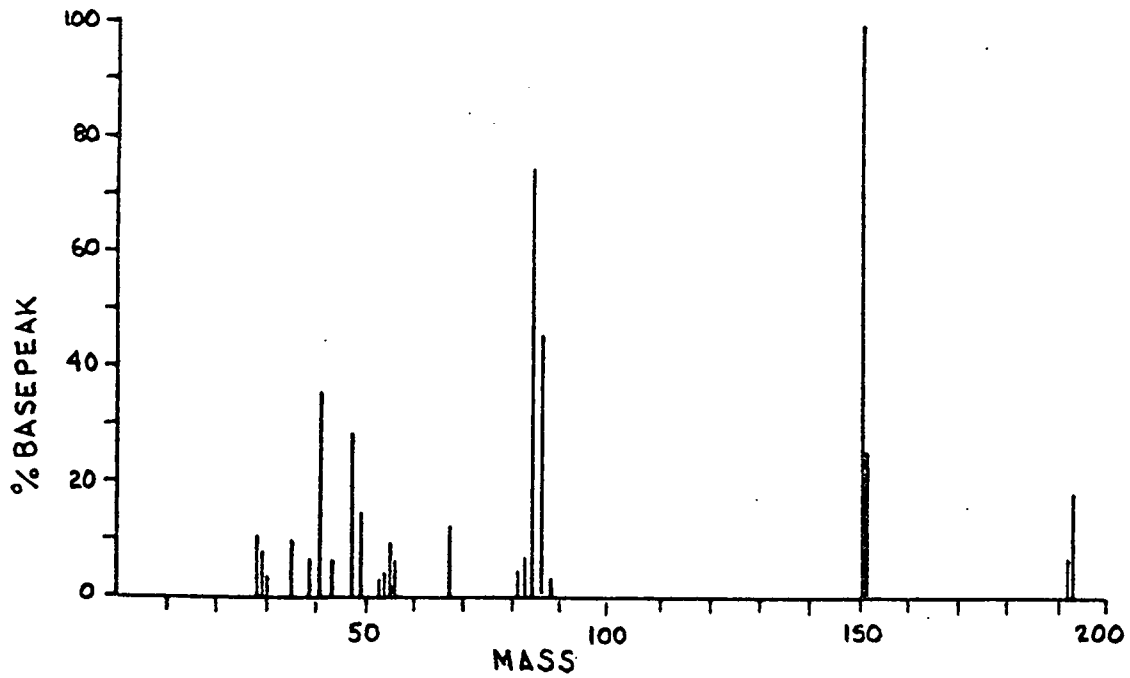


Figure 39. Mass Spectrum for perhydroacridine.

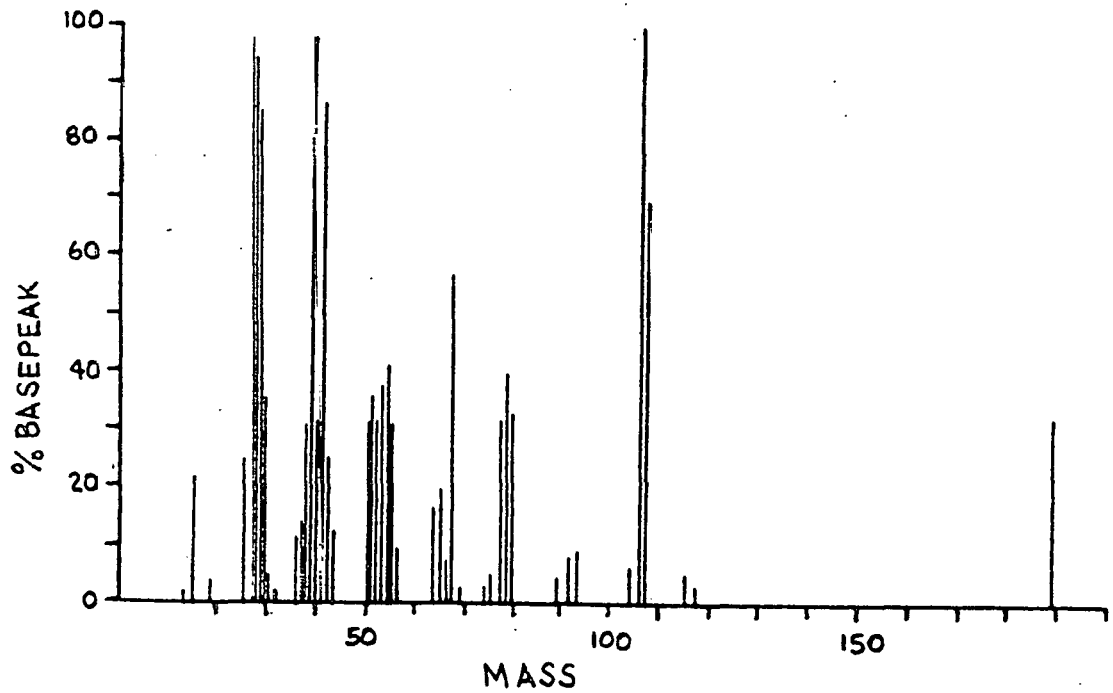


Figure 40. Mass Spectrum for o-(methylenecyclohexane)aniline.

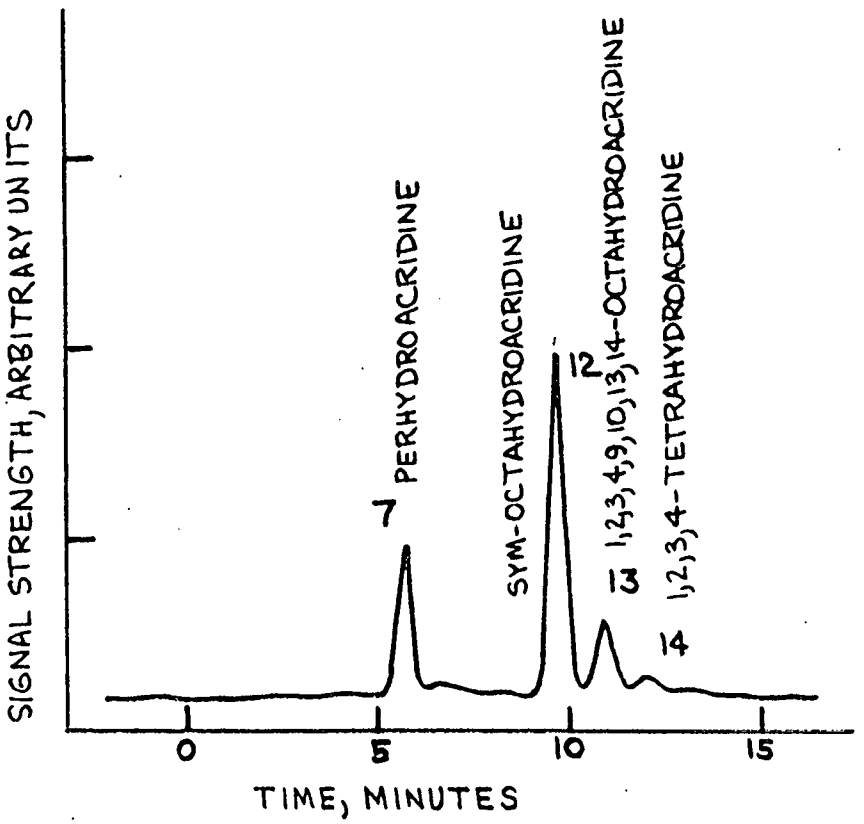


Figure 41. Chromatogram for an Acridine Reactor Sample: 353°C and 2000 psig (Run 1050 - 10 minutes); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) catalyst.

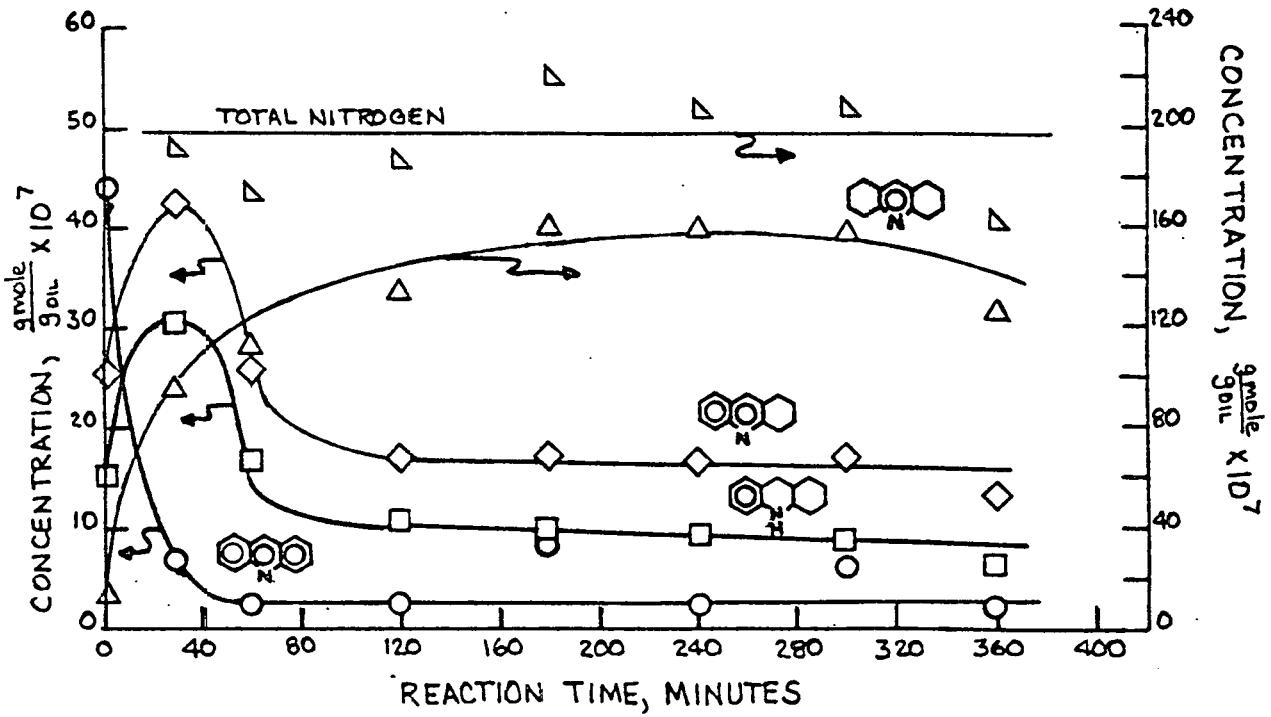


Figure 42. Concentration Profiles for Acridine Hydrodenitrogenation: 340°C and 500 psig (Run 1042); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

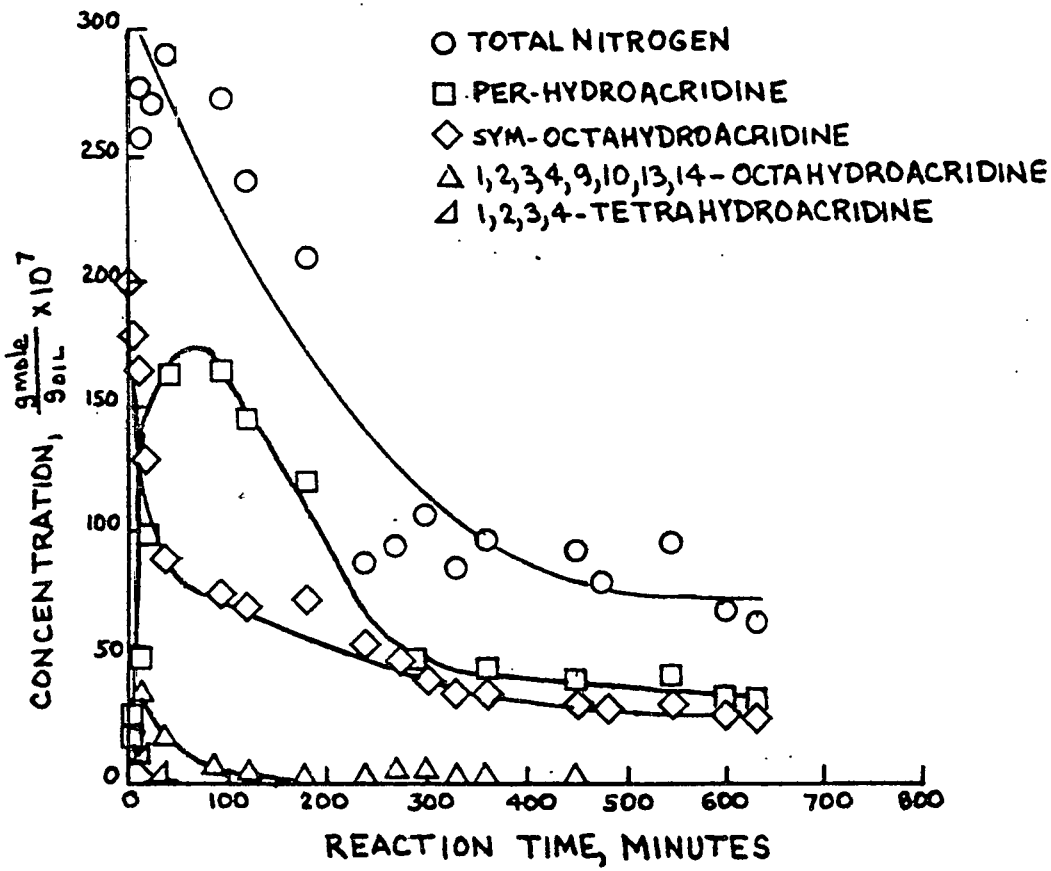


Figure 43. Concentration Profiles for Acridine Hydrodenitrogenation: 353°C and 2000 psig (Run 1050); Ni-Mo/Al_2O_3 (American Cyanimic HDS-9A) Catalyst.

tially no nitrogen is removed at 342°C and 500 psig (Run 1042) over a 360 minute period. However, the total nitrogen curve in Figure 43 indicates that there was a significant rate of nitrogen removal at 353°C and 2000 psig (Run 1050). Figure 44 presents a pseudo first-order kinetic analysis for the total nitrogen removal data for Run 1050 (353°C, 2000 psig). The rate constant was 0.51 $\frac{g_{oil}}{g_{catalyst}\text{-min}}$ and the coefficient of correlation was -0.918. Detailed concentration and reaction condition data for Runs 1042 and 1050 are presented in Appendix J. There were two experimental problems associates with Run 1050 (353°C, 2000 psig). First, the temperature rose at least 20°C above 353°C between the reaction sample taken at 180 and at 240 minutes. Second, all the acridine had undergone hydrogenation before the catalyst was injected into the reactor. Although all the acridine had undergone hydrogenation, there was no nitrogen removal since the measured total nitrogen concentration at zero time was the same as the amount of acridine initially loaded into the reactor. Figures 43 and 44 indicate that the initial reactor samples had this total nitrogen concentration. However, Run 1042

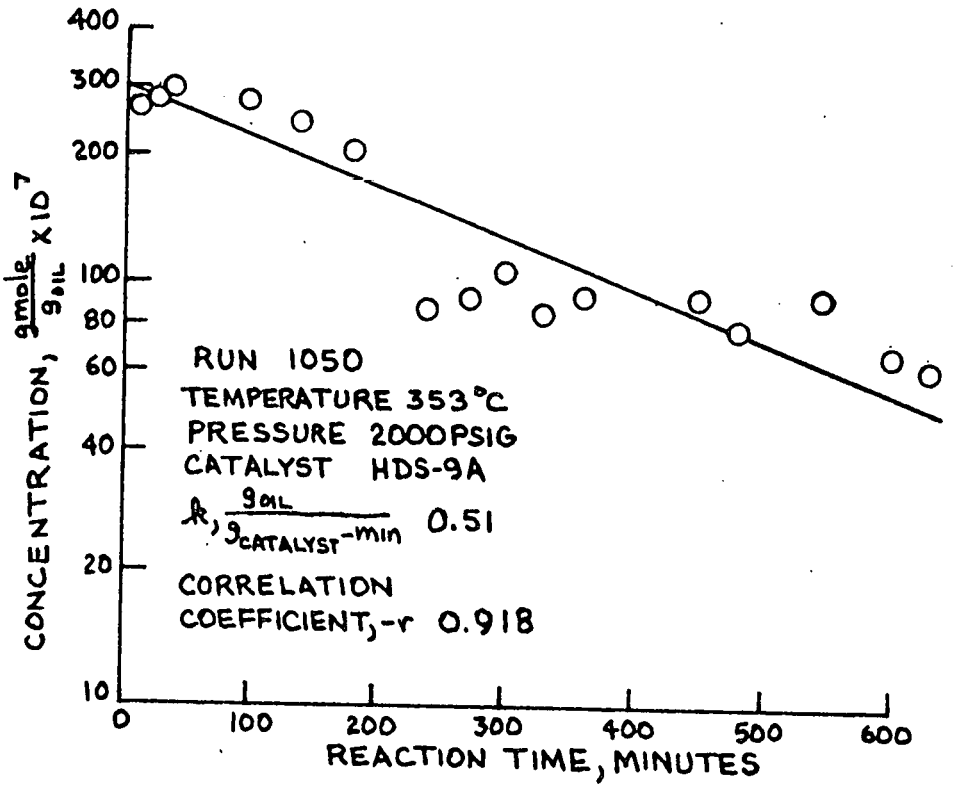


Figure 44. Pseudo First-order Kinetic Analysis for Total Nitrogen Removal: 353°C and 2000 psig (Run 1050); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

(342°C, 500 psig) had approximately the same initial acridine concentration loaded as Run 1050, and the total nitrogen curve in Figure 42 indicates only about one-fifth remained in the initial reactor samples. This difference is attributed to an error in the amount loaded; the important observation for this is the lack of nitrogen removal over a six hour period.

CHAPTER IV

DISCUSSION OF RESULTS

A. Hydrodenitrogenation of Quinoline

The blank reactor experiments indicated that the reactivity of quinoline is negligible in the absence of catalyst. Therefore, this experiment insured that the observed kinetics are a measure of catalyst activity and are not a result of thermal or wall-catalyzed reactions.

The extracted first-order rate constants describing the disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline were reproducible within 2%; however, reactor reprodubibility will be discussed further with respect to the mass transfer effects experiments.

The mass transfer effects experiments indicated the possibility of significant intraparticle mass transfer resistances for a catalyst particle size range of 90 to 275 μm and of significant gas-liquid mass transfer resistances for a stirring speed range

of 750 to 1250 rpm. The possibility of significant intraparticle mass transfer resistances is based on the fact that different catalyst particle sizes (90 μm versus 275 μm) led to pseudo first-order rate constants for the disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline which differed by slightly over 20%. Values of the Thiele modulus were 0.329 (275 μm), 0.057 (125 μm) and 0.030 (90 μm). Thus, the effectiveness factor calculations, which were based on the diffusion of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline, indicated there were no significant intraparticle mass transfer effects. This contradiction could be explained by poorer run to run reproducibility than was reported in the reactor reproducibility experiments. The contradiction could also be explained by questioning the validity of the effectiveness factor calculations. The disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline was shown to follow pseudo first-order kinetics quite well, and the effectiveness factor calculations were based on the premise that a power law, irreversible kinetic analysis is valid. If the estimate of the effective diffusivity was changed by 50% so as to

obtain a larger estimate of the Thiele modulus, the conclusions drawn from the effectiveness factor calculations would remain the same. Therefore, it appears that the effectiveness factor calculations are rather insensitive to the estimate of the effective diffusivity. This result may also imply that the experiments were conducted in an intrinsic kinetic regime far from significant diffusional effects. The possibility of significant gas-liquid mass transfer resistances is based on the fact that one experiment (Run 1015; 125 μm) in the catalyst particle size survey did not produce a rate constant for the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline that had an intermediary value with the experiments run with catalyst particle sizes of 90 μm and 275 μm (Runs 1016 and 1017). This was attributed to the lower stirring speed of Run 1015.

The statistical analysis (correlation coefficients) for the catalyst survey indicated that pseudo first-order kinetics represent the rate of removal of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline very well over the range 0 to 50% conversion; however, pseudo zero-order

kinetics also yield reasonable results. The reaction network for the hydrodenitrogenation of quinoline in the absence of carbon disulfide is shown in Figure 45. Shih (1976) completed experiments in which carbon disulfide was present in the reactor to maintain a sulfided catalyst and found a reaction network for quinoline as shown in Figure 46. The rate constants shown in Figure 46 are based on a pseudo first-order kinetic analysis. This network is similar to that reported by Goudriaan (1974). Figure 1 presents Goudriaan's reaction network. There are differences in the two proposed networks. Goudriaan found partially hydrogenated ring species, such as propylcyclohexene, and 1-amino-2-propylcyclohexene, present while Shih did not. Also, Shih proposed alternate routes for the hydrogenolysis of 1,2,3,4-tetrahydroquinoline involving n-propylaniline and gamma-phenylpropylamine; however, these compounds were never detected in a reactor mixture.

Figure 46 indicates that quinoline hydrogenates very quickly to form 1,2,3,4-tetrahydroquinoline, and equilibrium is established. Quinoline also hydrogenates at a measurable rate to 5,6,7,8-tetrahydro-

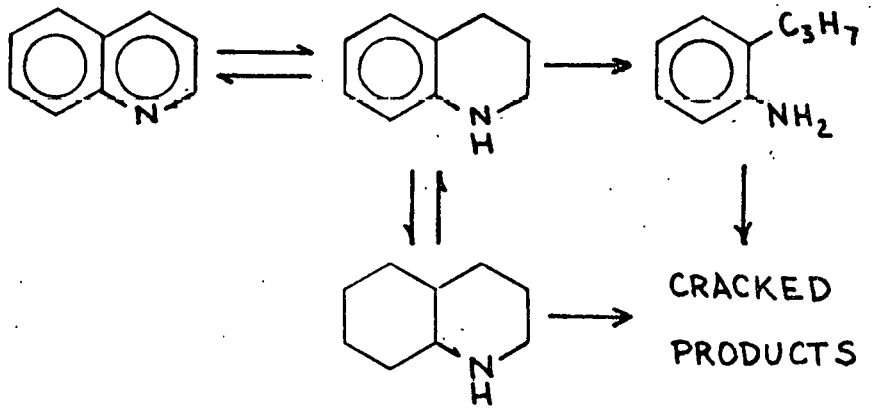
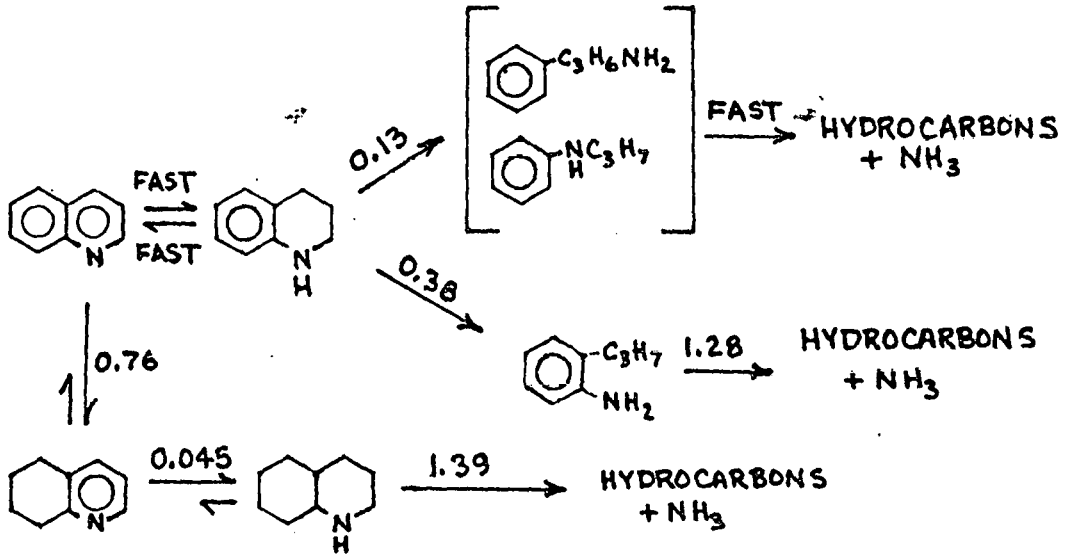


Figure 45. Quinoline Reaction Network in the Absence of Carbon Disulfide: 342°C and 500 psig; Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.



REACTION CONDITIONS

TEMPERATURE 342°C

PRESSURE 500 PSIG

INITIAL QUINOLINE CONCENTRATION 1.0 wt%

CATALYST HDS-9A (N_i-Mo/Al_2O_3)

CATALYST CONCENTRATION 2 g/500 cc oil

CS_2 CONCENTRATION 0.05 wt%

FIRST ORDER RATE CONSTANTS, $\frac{g_{OIL}}{g_{CATALYST}\text{-min.}}$

Figure 46. Quinoline Reaction Network in the Presence of Carbon Disulfide.

quinoline, which is very unreactive. Thus, for quinoline the hydrogenation of the nitrogen-containing ring is much faster than the hydrogenation of the benzene ring. This can be explained by the higher electronegativity of the nitrogen atom. Its unshared electrons increase the electron density and consequently activate the nitrogen-containing ring. Another explanation is that the basic nitrogen atom enhances adsorption of the nitrogen-containing ring on the catalyst surface and promotes hydrogenation of this ring. The steric hinderance arising from the (non-planar) puckered conformation of the saturated ring may create difficulties for adsorption on the catalyst surface, reduce the rate of adsorption, and thus retard activity.

The removal of nitrogen probably takes place via cracking of the saturated nitrogen-containing ring based on bond strength and resonance stabilization arguments. Roberts et al. (1971) report that the carbon-nitrogen single bond has an energy of 73 kcal/mole while the carbon-nitrogen double bond has an energy of 147 kcal/mole. Also, the reactivity of the aromatic nitrogen-containing ring should be

further reduced because of resonance stabilization.

Figure 46 shows that CS_2, when added to the reaction medium to maintain the catalyst in a sulfided state, promoted the formation of 5, 6,7,8-tetrahydroquinoline to a measurable concentration. This intermediate was not observed in the catalyst survey experiments in which CS_2 was not added to the reaction medium.

Another key point concerning Figure 46 is that the reaction time for the experiment was 13 hours. The concentration profiles of o-propylaniline and decahydroquinoline presented in Chapter III for the catalyst survey show that in a reaction time of 4 hours the concentrations of these compounds were still increasing and had not reached their maximum values. These concentrations should pass through a maximum and then decrease to allow a meaningful kinetic analysis to be performed to extract rate constants for the formation and depletion of these compounds. This was the case for the 13 hour experiment represented in Figure 46.

Figure 46 indicates that possibly the hydro-

genation of 5,6,7,8-tetrahydroquinoline to decahydroquinoline and the cracking of 1,2,3,4-tetrahydroquinoline are the rate-limiting steps. A summary of rate-limiting steps reported in the literature was presented in Table VII in Chapter I of this thesis. At approximately the same reaction conditions (350-400°C; 3000 psig) Aboul-Gheit and Abdou (1972) also found that the rate-limiting step was the cracking of 1,2,3,4-tetrahydroquinoline. Doelman and Vlugter (1963) found that the hydrogenolysis of o-propylaniline was rate-limiting, but they used pure quinoline as a reaction medium. More importantly, both of the above-mentioned studies used a cobalt-molybdenum catalyst while the results presented in Figure 46 were for a nickel-molybdenum catalyst. However, it should be noted that the concept of one discrete rate-limiting step for a reaction network containing several parallel and series steps is not always clear cut and definitive.

B. Hydrodenitrogenation of Acridine

The most difficult experimental problem concerning the hydrodenitrogenation of acridine was finding suitable and convenient gas chromatographic

conditions for the quantitative analysis of nitrogen-containing reaction products. This goal was never achieved using packed column technology (See Appendix F) and, therefore, many acridine reactor experiments which were performed were not analyzed and reported. It is hoped that future developmental work at the University of Delaware on the application of open tubular gas chromatographic columns will be successful in solving this problem. Recently, an OV-101 wall-coated capillary column has been found to be satisfactory for the acridine reaction sample analysis.

Of the 16 nitrogen-containing reaction products 6 were identified according to compound structure. A compound with a molecular weight of 201 indicates that alkyl transfer reactions can take place for acridine similar to that reported for quinoline by Goudriaan (1974). The problems associated with the identification of the reaction products using mass spectroscopy are described in Appendix H. A preliminary reaction network based on the six identified compounds is presented in Figure 47. Of the 16 nitrogen-containing compounds 5 compounds can be measured quantitatively in the reactor samples. These

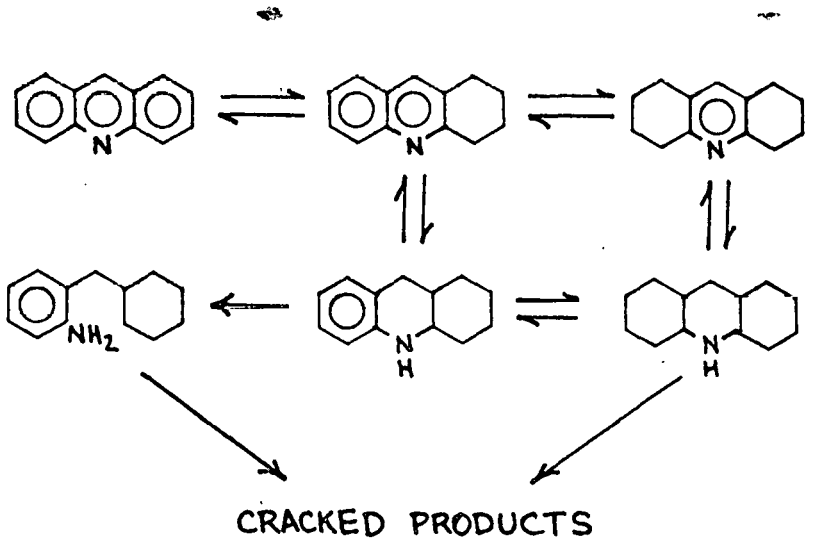


Figure 47. Preliminary Acridine Reaction Network: 353°C and 2000 psig (Run 1050); Ni-Mo/Al_2O_3 (American Cyanimid HDS-9A) Catalyst.

are acridine, 1,2,3,4-tetrahydroacridine, 1,2,3,4, 9,10,13,14-octahydroacridine, sym-octahydroacridine, and per-hydroacridine. The compounds assigned only a molecular weight are probably cracked products. Since the quinoline experiments indicated that compounds with partially hydrogenated aromatic rings were not formed, it is unlikely that compounds of this nature are present in the acridine experiments. At the experimental conditions of 340 to 355°C and 500 to 2000 psig o-(methylenecyclohexane)aniline appeared only in trace amounts in the reactor samples over a reaction time period of 12 hours. The other nitrogen-containing compounds assigned only a molecular weight appeared only in small quantities in the reaction samples and either were not detected or were fused with other major GC peaks.

The experiment (Run 1042) run at 340°C and 500 psig for 6 hours indicates that several species are probably in equilibrium (refer to Figure 42). After 80 minutes of reaction time the concentration ratio of 1,2,3,4-tetrahydroacridine to acridine is constant (6.3) and the ratio of 1,2,3,4-tetrahydroacridine to 1,2,3,4,9,10,13,14-octahydroacridine is

constant (1.7). Also, the concentration ratio of sym-octahydroacridine to 1,2,3,4-tetrahydroacridine is approximately constant (9.6), but there is more scatter in these data. The experiment run at 353°C and 2000 psig (Run 1050) for 12 hours did not show these trends; however, reactor samples taken before the injection of the catalyst indicated that acridine had essentially reacted completely to partially hydrogenated forms. This problem is serious with respect to calculating detailed kinetics for each species based on catalyst activity, and it was the impetus for the blank reactor (no catalyst) experiment, which has not been analyzed. A serious problem associated with Run 1042 (342°C, 500 psig) is that the total nitrogen content of the initial reactor samples taken shortly after injection of the catalyst was only 20% of the initial acridine concentration loaded into the reactor. However, regardless of this problem there was no total nitrogen removal over a 360 minute reaction time period for Run 1042 (refer to Figure 42).

The pseudo first-order kinetic analysis performed on the total nitrogen concentration for

Run 1052 (353°C, 2000 psig) led to a rate constant of 0.51 $\frac{g_{oil}}{g_{catalyst}\text{-min}}$, and the quinoline experiment run at 342°C and 500 psig (Runs 1021 and 1031) led to a total nitrogen removal rate constant of 0.41 $\frac{g_{oil}}{g_{catalyst}\text{-min}}$. Dr. Shih has conducted quinoline experiments at 342°C and 2000 psig which led to a total nitrogen removal rate constant of 0.76 $\frac{g_{oil}}{g_{catalyst}\text{-min}}$. These rate constants indicate that the total nitrogen removal rates for quinoline and for acridine are the same order of magnitude.

Since no nitrogen-containing cracked products for acridine rose to significant, measurable concentrations, it would appear that the cracking of hydrogenated species of acridine could be the rate-limiting step in the hydrodenitrogenation of acridine. This also implies the only significant cracking step probably involves perhydroacridine. The bond strength arguments used in the analysis of the quinoline experiments can be applied to the acridine experiments. The carbon-nitrogen single bond (73 kcal/mole) is weaker than the carbon-nitrogen double bond (147 kcal/mole). In the quinoline experiments no cracked products of decahydroquinoline were formed in measur-

able concentrations, and in the acridine experiments no cracked products of perhydroacridine were formed in measurable concentrations. Both of these compounds have only carbon-nitrogen single bonds, and any of their cracked products are probably very reactive. o-(methylenecyclohexane)aniline is less reactive than any cracked products of perhydroacridine because of resonance stabilization of the carbon-nitrogen bond with the aromatic ring. Therefore, since this compound was not formed in measurable concentrations in the acridine experiments, the cracking step through 1,2,3,4,9,10,13,14-octahydroacridine is not significant.

A catalyst with better hydrogenation capabilities would promote the formation of reactive carbon-nitrogen single bond compounds and, thus, increase the rate of acridine hydrodenitrogenation. However, this would increase hydrogen consumption. Therefore, a catalyst which could selectively crack the stronger carbon-nitrogen double bond without hydrogenating the aromatic ring would be better for industrial hydrodenitrogenation operations. Also, compounds such as decahydroquinoline and perhydroacridine are not

planar molecules and have several conformations. Steric hindrances can result which decrease the reactivity of these compounds. A catalyst which possibly has stronger adsorption capabilities to overcome these steric hindrances would improve its hydrodenitrogenation capabilities.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The reactor reproducibility was measured to be better than 2% based on a pseudo first-order kinetic analysis for the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline.

2. Effectiveness factor calculations for the quinoline experiments indicated that there were no significant catalyst pore diffusion effects for the catalyst particle size range of 90 μm to 275 μm; however, kinetic analyses on the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline indicated there were differences between the catalyst particle sizes. These experiments also indicated the possibility of significant external mass transfer effects in the autoclave stirring speed range of 500 to 1250 rpm.

3. Nitrogen-containing reaction products for quinoline hydrodenitrogenation at 342°C and 500 psig were 1,2,3,4-tetrahydroquinoline, o-propylaniline, and decahydroquinoline when the catalyst was presulfided but when no carbon disulfide was added to the reaction medium to maintain the catalyst in the fully sulfided state. In experiments with carbon disulfide present 5,6,7,8-tetrahydroquinoline was formed.

4. In quinoline hydrodenitrogenation at 342°C and 500 psig quinoline and 1,2,3,4-tetrahydroquinoline are in thermodynamic equilibrium.

5. The total nitrogen removal rate for quinoline follows pseudo first-order kinetics quite well over the 0 to 50% conversion range at 342°C and 500 psig. Pseudo zero-order kinetics fit almost as well.

6. The disappearance of the lumped group of quinoline plus 1,2,3,4-tetrahydroquinoline follows pseudo first-order kinetics.

7. For quinoline hydrodenitrogenation at 342°C and 500 psig the following ranking of catalysts in order of decreasing activity was observed: Ni-Mo/

Al_2O_3 (American Cyanimid HDS-9A), Ni-W/Al_2O_3 (NALCO NT-550), Ni-W/Al_2O_3 (Harshaw Ni4303), Ni-W/SiO_2-Al_2O_3 (Harshaw Ni4301), and Co-Mo/Al_2O_3 (American Cyanimid HDS-16A).

8. The presence of hydrogenated and partially hydrogenated reaction products probably implies that acridine must be hydrogenated before cracking and heteroatom removal occurs. This is supported by bond strength arguments which state that the carbon-nitrogen single bond is weaker than the carbon-nitrogen double bond.

9. The appearance of so many reaction products (16) for acridine hydrodenitrogenation implies that there are many paths possible for heteroatom removal. However, the most significant cracking step is probably through perhydroacridine. This is supported by bond strength arguments and by no significant measurable concentration of a cracked product in the reaction medium.

10. Identified nitrogen-containing reaction products for acridine hydrodenitrogenation were 1,2,3,4-tetrahydroacridine, 1,2,3,4,9,10,13,14-octa-

hydroacridine, sym-octahydroacridine, perhydroacridine, and o-(methylenecyclohexane)aniline. The presence of a reaction product with a molecular weight of 201 indicates that alkyl transfer reactions can occur.

11. A preliminary reaction network for acridine hydrodenitrogenation is presented (Figure 47, p.110).

12. Quinoline and acridine have total nitrogen removal rates which are the same order of magnitude.

13. The cracking of hydrogenated species of acridine is probably the rate-limiting step in the reaction network.

B. Recommendations

1. The reactor reproducibility for the 300 cc autoclave reactor should be studied further in a series of 3 to 5 experiments. If the reproducibility approaches 20%, then the effectiveness factor calculations are probably valid and no significant intraparticle mass transfer resistances are present in the catalyst particle size range of 90 to 275 μm. If the reactor reproducibility is much better than

20%, then the effectiveness factor calculations are suspect, and further experiments with smaller catalyst particle sizes (less than 90 μm) should be conducted to find a size region in which intraparticle mass transfer resistances are not significant.

2. A series of experiments should be made varying the autoclave reactor stirring speed in the 500 to 2000 rpm range to find a region in which varying the stirring speed does not effect the kinetic analysis.

3. For a fairer comparison catalysts should be prepared on supports of equivalent physical properties for evaluation of hydrodenitrogenation activity.

4. Catalyst parameters, such as metal content and physical properties, should be studied for their effect on the hydrogenation and cracking steps in the hydrodenitrogenation of acridine.

5. Other nitrogen-containing compounds such as substituted acridines and quinolines are desirable to study for their hydrodenitrogenation reactivity.

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APPENDIX A

DETAILED MATHEMATICS FOR THE PSEUDO FIRST-ORDER AND PSEUDO ZERO-ORDER KINETIC ANALYSES

PRESENTED BELOW ARE THE DETAILED MATHEMATICS FOR THE PSEUDO FIRST-ORDER AND THE PSEUDO ZERO-ORDER KINETIC ANALYSES.

FIRST-ORDER ANALYSIS

CONSIDER THE FOLLOWING RATE EXPRESSION DESCRIBING THE DISAPPEARANCE OF THE LUMPED GROUP OF QUINOLINE PLUS 1,2,3,4-TETRAHYDROQUINOLINE

$$r = k'[C][H]^{a}[Q+THQ]$$

WHERE

r = RATE OF REACTION, $\dfrac{\text{moles Q+THQ}}{g_{OIL}\text{-MINUTE}}$

k' = RATE CONSTANT, $\dfrac{[g_{OIL}]^2}{[\text{mole hydrogen}][g_{CATALYST}][\text{MINUTE}]}$

$[H]$ = HYDROGEN (H_2) CONCENTRATION, $\dfrac{\text{mole hydrogen}}{g_{OIL}}$

a = UNKNOWN CONSTANT

$[C]$ = CATALYST CONCENTRATION, $\frac{g_{CATALYST}}{g_{OIL}}$

$[Q+THQ]$ = CONCENTRATION OF QUINOLINE PLUS 1,2,3,4-TETRAHYDROQUINOLINE, $\frac{moles}{g_{OIL}}$

ASSUMING THAT THE HYDROGEN CONCENTRATION IS ESSENTIALLY CONSTANT IT CAN BE LUMPED WITH THE RATE CONSTANT TO OBTAIN

$$k'[H]^a \equiv k$$

$$r = k[C][THQ+Q]$$

ASSUMING AN IDEAL BATCH REACTOR

$$\frac{d[Q+THQ]}{dt} = -k[C][THQ+Q]$$

$$\int_{[Q+THQ]_0}^{[Q+THQ]} \frac{d[Q+THQ]}{[Q+THQ]} = -\int_0^t k[C]\,dt$$

$$\ln[Q+THQ] = -k[C]t + \ln[Q+THQ]_0$$

WHICH IS IN THE FORM

$$y = Ax + B$$

AND THUS A LINEAR REGRESSION ANALYSIS CAN BE APPLIED TO OBTAIN ESTIMATES OF THE PSEUDO FIRST-ORDER RATE CONSTANT, k, AND THE INITIAL CONCENTRATION, $[Q+THQ]_0$ . .

ZERO-ORDER ANALYSIS

CONSIDER THE FOLLOWING RATE EXPRESSION DESCRIBING THE DISAPPEARANCE OF THE LUMPED GROUP OF QUINOLINE PLUS 1,2,3,4-TETRAHYDROQUINOLINE

$$r = k'[H]^a \equiv k$$

AGAIN, ASSUMING IDEAL BATCH REACTOR BEHAVIOR

$$\frac{d[Q+THQ]}{dt} = -k$$

INTEGRATING

$$[Q+THQ] = -kt + [Q+THQ]_0$$

WHICH IS IN THE FORM

$$y = Ax + B$$

AGAIN, A LINEAR REGRESSION ANALYSIS CAN BE APPLIED TO OBTAIN ESTIMATES OF k AND $[Q+THQ]_0$.

APPENDIX B

CONCENTRATION PROFILES FOR REACTOR REPRODUCIBILITY EXPERIMENTS

DATE OF ANALYSIS 2/16/76

RUN 1020

COMPOUND			 "Q"	 "THQ"	TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.0	6.9	8.7	11.6	—	—	—				¢
CONC. UNITS	$\frac{gmole}{g_{oil}} \times 10^{7}$	$\frac{gmole}{g_{oil}} \times 10^{7}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	—				
SAMPLE #											
2	—	—	19.1	43.9	63.0	63.0	2.3				
5	8.84	—	6.62	58.3	65.8	65.8	8.8				
10	22.4	12.5	4.92	58.0	66.5	62.9	11.8				
15	29.2	17.1	6.43	44.9	61.0	56.3	7.9				
30	48.2	38.2	6.60	46.3	61.6	52.9	7.0				
60	68.2	63.5	5.27	41.5	59.9	46.8	7.9				
90	82.2	78.5	4.29	34.8	55.2	39.1	8.1				
120	89.4	94.0	3.67	31.0	53.0	34.7	8.5				
150	95.5	109	3.69	29.5	53.6	33.2	8.0				
180	86.8	99.8	2.99	22.2	43.9	25.2	7.4				
210	90.1	102	2.62	20.2	42.0	22.8	7.7				

RUN CONDITIONS:

TEMPERATURE, ℃ 343
PRESSURE, PSIG 500
CATALYST HDS-9A
CATALYST CONC. 2g/500cc
CATALYST SIZE 125μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 64.7×10^{-6} gmole/g$_{oil}$
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 4/12/76 RUN 1031

COMPOUND			 "Q"		TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.3	6.9	8.6	11.2	—	—	—				
CONC. UNITS	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	—				
SAMPLE #											
2	12.7	12.9	8.34	54.6	65.5	62.9	6.5				
5	32.1	20.7	6.10	44.9	61.3	56.0	8.2				
15	57.1	39.5	7.16	52.1	68.9	59.2	7.3				
30	69.3	48.3	5.53	41.3	58.6	46.8	7.5				
60	93.7	76.5	5.09	33.8	61.5	43.9	7.6				
93	104	85.1	4.62	31.3	55.0	36.0	6.8				
120	105	88.6	3.97	26.8	50.1	30.8	6.8				
180	115	99.5	3.01	22.0	46.4	25.0	7.3				

RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-9A
CATALYST CONC. 2g/500cc oil
CATALYST SIZE 125 μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 67.4×10^{-6} gmole/g$_{OIL}$
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

APPENDIX C

EFFECTIVENESS FACTOR CALCULATIONS

THE EFFECTIVENESS FACTOR CALCULATIONS WERE BASED ON THE METHODOLOGY DESCRIBED IN MASS TRANSFER IN HETEROGENEOUS CATALYSIS BY C.N. SATTERFIELD. ALL PAGE NUMBER CITATIONS IN THIS APPENDIX REFER TO THIS BOOK.

THE EFFECTIVENESS FACTOR CALCULATIONS ARE BASED ON THE DISAPPEARANCE OF THE LUMPED GROUP OF QUINOLINE PLUS 1,2,3,4-TETRAHYDRO-QUINOLINE. EXPERIMENTAL DATA HAVE BEEN SHOWN TO FOLLOW PSEUDO FIRST-ORDER KINETICS.

FIRST, THE MOLECULAR DIFFUSIVITY FOR 1,2,3,4-TETRA-HYDROQUINOLINE IN WHITE OIL AT 342°C MUST BE ESTIMATED.

p.18 STOKES-EINSTEIN CORRELATION $$D_{12} = \frac{1.05 \times 10^{-9} T}{\mu V_b^{1/3}}$$

FOR 1,2,3,4-TETRAHYDROQUINOLINE (THQ)

$$(V_b)_{THQ} = 6(V_b)_{CARBON} + 11(V_b)_{HYDROGEN} + 1(V_b)_{NITROGEN} - (30)_{NAPHTHALENE\ RING\ STRUCTURE}$$

$$= 111.50$$

$$D_{THQ} = \frac{[1.05 \times 10^{-9}][342+273\,^{\circ}K]}{[0.00256][111.5]^{1/3}} = 5.24 \times 10^{-5}\ \frac{cm^2}{sec}$$

NOTE: THE VISCOSITY (μ) AND MOLECULAR WEIGHT OF WHITE OIL AT 342°C WERE ESTIMATED BY THOMAS' METHOD AND BY ASSUMPTION OF A $C_{24}H_{50}$ PARAFFIN, RESPECTIVELY.

SINCE THE CATALYST PROPERTIES WERE NOT AVAILABLE FOR AMERICAN CYANIMID'S HDS-16A CATALYST, IT WAS ASSUMED THAT HDS-16A HAD SIMILAR PROPERTIES OF HDS-3 CATALYST, A NICKEL-MOLY AMERICAN CYANIMID CATALYST

PORE VOLUME 0.6 $^{cc}/_{g}$

SURFACE AREA 180 $^{m^2}/_{g}$

COMPACTED BULK DENSITY 43 $^{lb}/_{ft^3}$

p. 66

τ = TORTUOSITY FACTOR $\cong$ 4.75

θ = VOLUME FRACTION VOIDS $\cong$ 0.354

SO THAT THE EFFECTIVE DIFFUSIVITY BECOMES

$$D_{THQ_E} = \frac{D_{THQ}\,\theta}{\tau} = 3.91 \times 10^{-6}\ cm^2/sec$$

NEXT, THE THIELE MODULUS CALCULATION

p.142 $$\phi_s = \frac{R^2}{D_E}\left(-\frac{1}{V_c}\frac{dn}{dt}\right)\frac{1}{C_s}$$ FOR SPHERICAL GEOMETRY

ϕ_s = THIELE MODULUS

R = CATALYST RADIUS

V_c = CATALYST VOLUME

dn/dt = RATE OF REACTION, gmoles/sec

C_s = REACTANT CONCENTRATION @ CATALYST SURFACE

BASED ON 0.8g CATALYST LOADED IN REACTOR

$$V_c = \frac{0.8g}{0.8\ g/cc} = 1.0\ cc$$

RUN 1015 (125 μm)

ESTIMATE OF dn/dt

FROM APPENDIX D

@ t=7min $[Q+THQ] = 60.04 \times 10^{-6} \frac{gmole}{goil}$

@ t=90min $[Q+THQ] = 54.08 \times 10^{-6} \frac{gmole}{goil}$

$$\frac{dn}{dt} \cong \frac{(60.04-54.08)\times 10^{-6} \frac{gmole}{goil}}{(7-90\,min)(60\,sec/min)} (210\,cc)(0.834\,g/cc)$$

$$= -2.096 \times 10^{-7}\ gmole/sec$$

$$C_s = \frac{(60.04+54.08)\times 10^{-6} \frac{gmole}{goil}}{2} (0.648\,g/cc) = 3.697 \times 10^{-5} \frac{gmole}{cc}$$

$$R \cong \frac{125 \times 10^{-6}\,m}{2} (10^2\,cm/m) = 62.5 \times 10^{-4}\,cm$$

$$\phi_s = \frac{(62.5\times 10^{-4}\,cm)^2}{(3.91\times 10^{-6}\,cm^2/sec)} \left[-\frac{1}{(1.0\alpha)}(-2.096\times 10^{-7} \frac{gmole}{sec})\right] \frac{1}{(3.697\times 10^{-5} \frac{gmole}{cc})}$$

$$= 0.057$$

p. 144 FIGURE 3.5 $\eta \cong 1.0$

RUN 1016 (275 μm)

$$\frac{dn}{dt} \cong \frac{(59.94-52.88)\times10^{-6}}{(5-90)\,min\,(60\,sec/min)}(210)(0.834)$$

$$= -2.424\times10^{-7}\ \frac{gmole}{sec}$$

$$C_s \cong 3.655\times10^{-5}\ gmole/cc$$

$$R \cong 138\times10^{-4}\ cm$$

$$\phi_s = \frac{(138\times10^{-4})^2}{(3.91\times10^{-6})}\left[-\frac{1}{1.0}(2.424\times10^{-7})\right]\left[\frac{1}{3.655\times10^{-5}}\right] = 0.329$$

p144 FIGURE 3.5 $\eta \cong 1.0$

RUN 1017 (90 μm)

$$\frac{dn}{dt} \cong \frac{(58.27-64.49)\times10^{-6}}{(90-10)(60)}(210)(0.834) = -2.270\times10^{-7}\ \frac{gmole}{sec}$$

$$C_s \cong 3.977\times10^{-5}\ \frac{gmole}{cc}$$

$$R \cong 45\times10^{-4}\ cm$$

$$\phi_s = 0.030$$

p144 FIGURE 3.5 $\eta \cong 1.0$

APPENDIX D

CONCENTRATION PROFILES FOR CATALYST PARTICLE SIZE SURVEY

COMPOUND					TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.5	7.6	9.6	12.8	—	—	—				
CONC. UNITS	$\frac{\text{gmole}}{\text{gm}} \times 10^7$	$\frac{\text{gmole}}{\text{gm}} \times 10^7$	$\frac{\text{gmole}}{\text{gm}} \times 10^6$	$\frac{\text{gmole}}{\text{gm}} \times 10^6$	$\frac{\text{gmole}}{\text{gm}} \times 10^6$	$\frac{\text{gmole}}{\text{gm}} \times 10^6$	—				
SAMPLE #											
2	—	—	47.9	13.3	61.2	61.2	0.28				
5	2.74	—	35.8	22.1	58.1	57.8	0.62				
7	—	—	31.1	28.9	60.0	60.0	0.93				
10	3.13	7.05	25.5	35.7	62.3	61.2	1.4				
15	5.48	9.07	19.2	39.8	60.5	59.0	2.1				
30	8.49	17.5	11.7	48.0	62.4	59.8	4.1				
45	13.2	22.0	9.10	48.6	61.2	57.7	5.3				
60	15.3	27.0	9.28	47.5	61.0	56.8	5.1				
75	17.2	29.3	7.96	46.1	58.7	54.0	5.9				
90	20.1	35.0	7.74	46.3	58.6	54.1	6.0				
120	23.3	36.9	6.74	43.4	56.1	50.1	6.4				
150	27.1	42.1	6.67	42.3	55.9	49.0	6.3				
180	29.2	47.7	6.16	40.6	54.5	46.8	6.6				
210	33.6	54.7	6.08	39.7	54.6	45.8	6.5				

DATE OF ANALYSIS 3/3/76

RUN 1015

RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-16A
CATALYST CONC. 20/500cc
CATALYST SIZE 125/μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 67.7×10^{-6} gmole/gm
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 3/3/76 RUN 1016

COMPOUND			 "Q"	 "THQ"	TOTAL NITROGEN	Q + THQ	THQ/Q
RET. TIME	4.5	7.6	9.6	12.8	—	—	—
CONC. UNITS	$\frac{\text{gmole}}{g_{soln}} \times 10^7$	$\frac{\text{gmole}}{g_{soln}} \times 10^7$	$\frac{\text{gmole}}{g_{soln}} \times 10^6$	$\frac{\text{gmole}}{g_{soln}} \times 10^6$	$\frac{\text{gmole}}{g_{soln}} \times 10^6$	$\frac{\text{gmole}}{g_{soln}} \times 10^6$	—
SAMPLE #							
2	—	—	52.2	9.77	61.9	61.9	0.19
5	—	—	39.3	20.6	59.9	59.9	0.53
10	5.00	7.74	25.5	33.3	60.1	58.8	1.3
15	7.59	12.4	19.1	41.8	63.0	61.0	2.2
30	10.5	22.1	11.0	46.8	61.1	57.8	4.3
45	14.9	31.0	9.69	45.8	60.1	55.5	4.7
60	20.5	37.0	8.62	47.4	61.7	56.0	5.5
75	21.1	40.7	8.36	43.7	58.2	52.1	5.2
90	27.0	49.0	9.48	43.4	60.5	52.9	4.6
120	23.3	56.5	7.24	41.6	57.3	48.9	5.8
150	33.4	58.2	5.91	39.8	54.8	45.6	6.7
180	39.5	64.7	5.97	39.5	55.9	45.4	6.6
210	42.7	67.8	5.46	36.5	53.0	41.9	6.7

RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-16A
CATALYST CONC. 20/500cc
CATALYST SIZE 275/um

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED)
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 3/4/76 RUN 1017

COMPOUND					TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.9	7.6	9.6	12.5	—	—	—				
CONC. UNITS	$\frac{g\,mole}{g_{oil}} \times 10^{7}$	$\frac{g\,mole}{g_{oil}} \times 10^{7}$	$\frac{g\,mole}{g_{oil}} \times 10^{6}$	$\frac{g\,mole}{g_{oil}} \times 10^{6}$	$\frac{g\,mole}{g_{oil}} \times 10^{5}$	$\frac{g\,mole}{g_{oil}} \times 10^{6}$	—				
SAMPLE #											
2	—	—	43.1	19.5	62.6	62.6	0.45				
5	1.30	1.59	18.4	44.5	63.1	62.8	2.4				
10	7.22	8.43	9.51	55.0	66.1	64.5	5.8				
15	12.3	11.0	8.93	57.0	68.3	65.9	6.3				
20	12.0	12.1	8.50	49.9	60.8	58.3	5.9				
30	17.6	21.3	8.27	52.9	65.1	61.2	6.4				
45	23.3	31.0	6.78	53.5	67.7	62.3	6.1				
60	25.1	29.8	7.68	46.9	60.0	54.5	6.1				
90	35.4	42.0	7.65	50.6	66.1	58.3	6.6				
120	39.3	49.7	7.40	45.8	62.1	53.2	6.2				
155	44.3	57.0	6.71	44.0	60.8	50.7	6.6				
135	48.3	68.4	7.02	42.6	61.3	49.6	6.1				
210	49.7	67.1	5.85	40.9	58.4	46.7	7.0				

RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-16A
CATALYST CONC. 2g/500cc oil
CATALYST SIZE 90 μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 66.5×10^{-6} g mole/g oil
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

APPENDIX E

CONCENTRATION PROFILES FOR CATALYST SURVEY

DATE OF ANALYSIS 3/4/76 RUN 1017

COMPOUND					TOTAL NITROGEN	Q + THQ	THQ/Q				
RET TIME	4.9	7.6	9.6	12.8	—	—	—				
CONC. UNITS	$\frac{\text{gmole}}{\text{cc oil}} \times 10^{7}$	$\frac{\text{gmole}}{\text{gm oil}} \times 10^{7}$	$\frac{\text{gmole N}}{\text{gm oil}} \times 10^{6}$	$\frac{\text{gmole}}{\text{gm oil}} \times 10^{6}$	$\frac{\text{gmole}}{\text{cc oil}} \times 10^{5}$	$\frac{\text{gmole}}{\text{cc oil}} \times 10^{5}$	—				
SAMPLE #											
2	—	—	43.1	19.5	62.6	62.6	0.45				
5	1.30	1.55	18.4	44.5	63.1	62.8	2.4				
10	7.22	8.43	9.51	55.0	66.1	64.5	5.8				
15	12.3	11.0	8.98	57.0	68.5	65.9	6.3				
20	12.0	12.1	8.50	48.9	60.6	58.3	5.9				
30	17.6	21.3	8.27	52.8	65.1	61.2	5.4				
45	22.3	31.0	8.78	53.5	67.7	62.3	6.1				
60	25.1	29.8	7.68	46.9	60.0	54.5	6.1				
90	35.4	43.0	7.65	50.6	66.1	58.3	6.6				
120	39.3	49.7	7.40	45.8	62.1	53.2	6.2				
155	44.3	57.0	6.71	44.0	60.8	50.7	6.6				
185	48.3	63.4	7.02	42.6	61.3	49.6	6.1				
210	49.7	67.1	5.85	40.9	58.4	46.7	7.0				

RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-16A
CATALYST CONC. 2g/500cc oil
CATALYST SIZE 90 μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 66.5×10^{-6} gmole/gm
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 2/18/76 RUN 1020

COMPOUND			 "Q"	 "THQ"	TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.0	6.9	8.7	11.6	—	—	—				
CONC. UNITS	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	—				
SAMPLE #											
2	—	—	19.1	43.9	63.0	63.0	2.3				
5	8.84	—	6.62	58.3	65.8	65.8	8.8				
10	22.4	12.5	4.92	58.0	66.5	62.9	11.8				
15	29.2	17.1	6.43	44.9	61.0	56.3	7.8				
30	48.2	38.2	6.60	46.3	61.6	52.9	7.0				
60	68.2	63.5	5.27	41.5	59.9	46.8	7.9				
90	82.2	78.5	4.29	34.8	55.2	39.1	8.1				
120	89.4	94.0	3.67	31.0	53.0	34.7	8.5				
150	95.5	109	3.69	29.5	53.6	33.2	8.0				
180	86.8	99.8	2.99	22.2	43.9	25.2	7.4				
210	90.1	102	2.62	20.2	42.0	22.8	7.7				

RUN CONDITIONS:

TEMPERATURE, °C 343
PRESSURE, PSIG 500
CATALYST HDS-9A
CATALYST CONC. 2 g/500 oil
CATALYST SIZE 125 μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 64.7×10^{-6} $\frac{gmole}{g_{OIL}}$
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

INITIAL OIL ANALYSIS 2/25/76 RUN 1021

COMPOUND			 Q	 THQ	TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.8	7.9	9.9	13.3	—	—	—				
CONC. UNITS	$\frac{\text{gmole}}{g_{oil}} \times 10^{7}$	$\frac{\text{gmole}}{g_{oil}} \times 10^{7}$	$\frac{\text{gmole}}{g_{oil}} \times 10^{6}$	$\frac{\text{gmole}}{g_{oil}} \times 10^{6}$	$\frac{\text{gmole}}{g_{oil}} \times 10^{6}$	$\frac{\text{gmole}}{g_{oil}} \times 10^{6}$	—				
SAMPLE #											
2	—	—	50.4	15.3	65.7	65.7	0.30				
5	2.68	—	24.9	36.7	61.9	61.6	1.5				
10	10.9	12.7	12.9	47.1	62.4	60.1	3.6				
22	25.5	21.9	7.26	53.9	65.9	61.1	7.4				
35	36.0	29.4	6.97	48.7	62.2	55.6	7.0				
61	50.1	42.4	7.30	44.2	60.8	51.5	6.1				
90	61.5	59.3	8.10	42.8	63.0	50.9	5.3				
117	72.1	68.9	6.40	39.2	59.7	45.6	6.1				
159	80.4	85.0	6.39	34.8	57.7	41.2	5.4				
210	89.9	108.5	5.96	31.0	56.8	36.9	5.2				

RUN CONDITIONS:

TEMPERATURE, °C 341
PRESSURE, PSIG 500
CATALYST HERSHAW Ni 4301
CATALYST CONC. 20/500 cc oil
CATALYST SIZE 125/μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 67.6×10^{-6} gmole/goil
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 3/9/76 RUN 1022

COMPOUND			Q	THQ	TOTAL NITROGEN	Q + THQ	THQ/Q				
RET. TIME	4.6	7.6	9.5	12.8	—	—	—				
CONC. UNITS	$\frac{gmole}{g_{oil}} \times 10^{7}$	$\frac{gmole}{g_{oil}} \times 10^{7}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	$\frac{gmole}{g_{oil}} \times 10^{6}$	—				
SAMPLE #											
2	5.78	—	46.7	25.0	69.3	68.7	0.57				
5	9.36	—	24.6	47.0	72.5	71.6	1.9				
10	12.0	10.9	10.9	43.1	61.3	59.0	4.4				
20	24.6	23.1	8.16	50.3	63.2	58.4	6.2				
30	38.9	34.5	9.06	53.7	70.1	62.7	5.9				
60	53.8	55.7	7.74	46.1	64.8	53.8	6.0				
90	62.5	77.5	8.10	42.2	66.3	50.3	5.2				
120	72.5	90.5	6.88	38.3	61.5	45.2	5.6				
150	75.8	105	6.77	34.5	59.4	41.3	5.1				
183	83.5	120	5.93	33.5	59.8	39.5	5.7				
210	82.5	120	5.22	27.4	52.9	32.7	5.3				

RUN CONDITIONS:

TEMPERATURE, °C 343
PRESSURE, PSIG 500
CATALYST Ni-4303
CATALYST CONC. 2/500cc OIL
CATALYST SIZE 125/149

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 68.2×10^{-6} gmole/g_{oil}
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

DATE OF ANALYSIS 3/17/76 RUN 1023

COMPOUND			 Q		TOTAL NITROGEN	Q + THQ	THQ/Q				
RET TIME	4.6	7.6	9.5	12.3	—	—	—				
CONC. UNITS	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{7}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{5}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	$\frac{gmole}{g_{OIL}} \times 10^{6}$	—				
SAMPLE #											
2	—	—	31.8	31.0	62.7	62.7	0.97				
5	5.83	7.39	11.9	48.2	61.3	60.0	4.1				
10	15.1	12.8	7.29	51.9	62.0	59.2	7.1				
25	31.1	27.9	6.66	47.5	60.1	54.2	7.1				
40	35.9	37.8	7.09	42.0	54.5	49.1	5.9				
60	41.4	61.1	8.48	38.1	56.9	46.6	4.5				
90	51.8	79.0	5.55	34.8	53.5	40.4	6.3				
110	59.6	94.1	5.40	32.7	53.4	38.1	6.1				
150	65.1	104	4.70	26.9	48.5	31.6	5.7				
180	71.4	112	3.95	24.1	46.4	28.1	6.1				

RUN CONDITIONS:

TEMPERATURE, °C 344
PRESSURE, PSIG 520
CATALYST NT-550
CATALYST CONC. 2g/50cc OIL
CATALYST SIZE 125 μm

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 67.7×10^{-6} gmole/g OIL
CS_2 CONC. (LOADED) NONE
H_2S GAS PHASE CONC. TRACE

APPENDIX F

ANALYTICAL PROBLEMS WITH THE GAS CHROMATOGRAPHIC ANALYSIS OF NITROGEN-CONTAINING ACRIDINE REACTION PRODUCTS

This work concerned the development of suitable gas chromatographic conditions (stationary phase, temperature, flowrate) for the quantitative analysis of nitrogen-containing acridine reaction products using a Perkin-Elmer 3920B gas chromatograph with a nitrogen specific detector. Many different stationary phases were investigated and rejected for various reasons. Table A-F-I presents a list of some of the stationary phases investigated and a summary of the reasons for rejection. Figures A-F-1 through A-F-5 present chromatograms on several stationary phases for an acridine reaction sample.

There were several reasons for rejecting a stationary phase. First the acridine reaction sample was known to have at least five major compounds, and the stationary phase should be capable of having these well-resolved. Second, the compound peak shapes should approach a Gaussian distribution and, therefore,

TABLE A-F-I

STATIONARY PHASES INVESTIGATED FOR THE ANALYSIS OF NITROGEN-CONTAINING REACTION PRODUCTS

Stationary Phase	Column*	Thermal Limit, °C	Reasons for Rejection
Apiezon L (2% KOH) on 80/100 Chromosorb WAW	6' X 1/8" SS	225	Resolution
SAME AS ABOVE	17' X 1/8" SS	225	Detector Sensivity
SAME AS ABOVE	5' X 1/8" G	225	Resolution
60/80 Chromosorb-103	5' X 1/8" SS	300	Resolution, excessive retention times
SAME AS ABOVE	6' X 1/8" SS	300	SAME AS ABOVE
SAME AS ABOVE	5' X 1/8" G	300	SAME AS ABOVE
10% UC-W98	6' X 1/8" SS	250	Resolution, slight tailing
Carbowax 20M (2% KOH) on Chromosorb WAW	10' X 1/8" SS	225	Resolution, tailing
Tenax	6' X 1/8" SS	375	Resolution

G = Glass column
SS = Stainless steel column

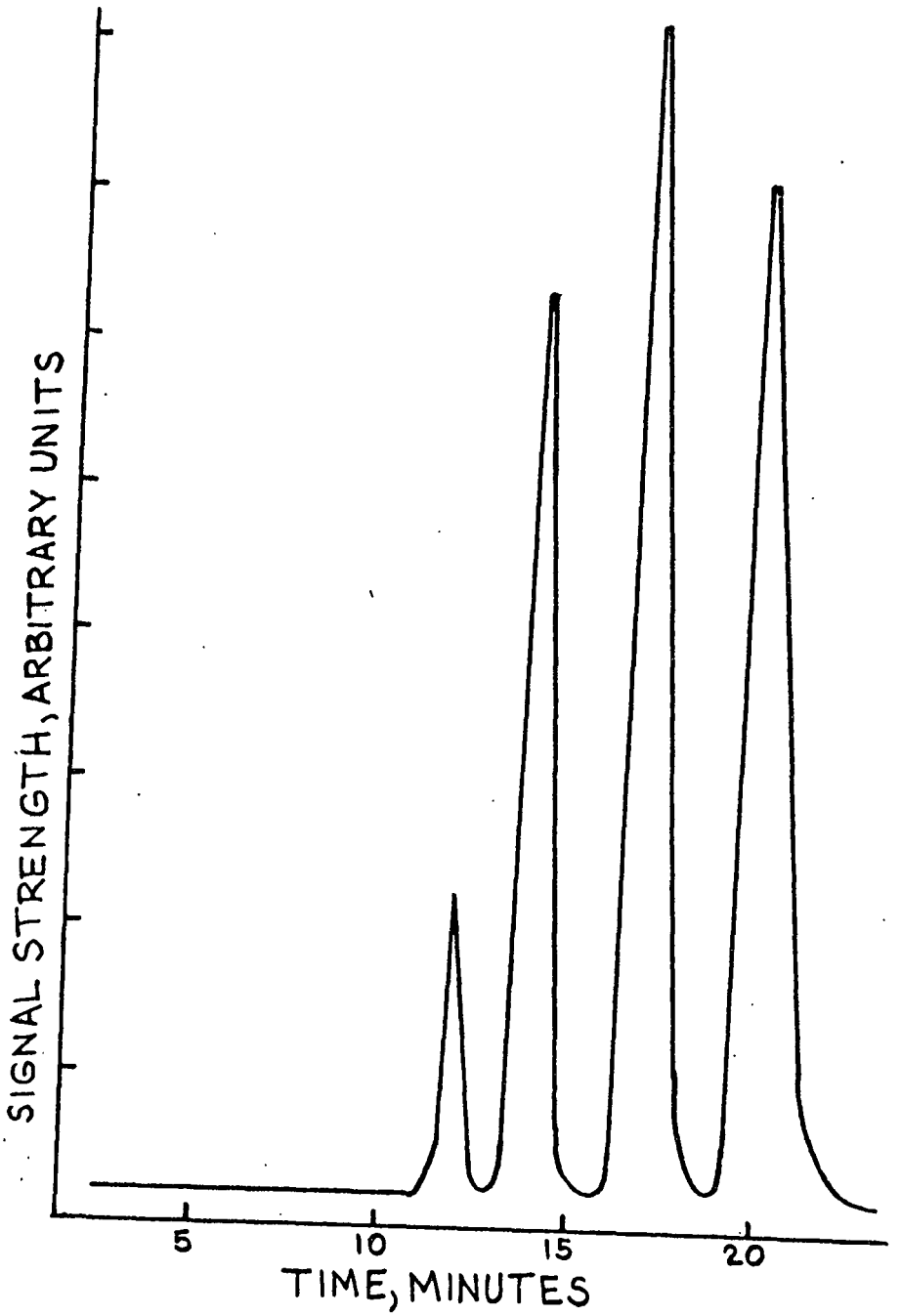


Figure A-F-1. Chromatogram of Acridine Reaction Sample (Run 1041-10) on a 5' X 1/8" Apiezon L (2% KOH): 180°C, 30 cc/min.

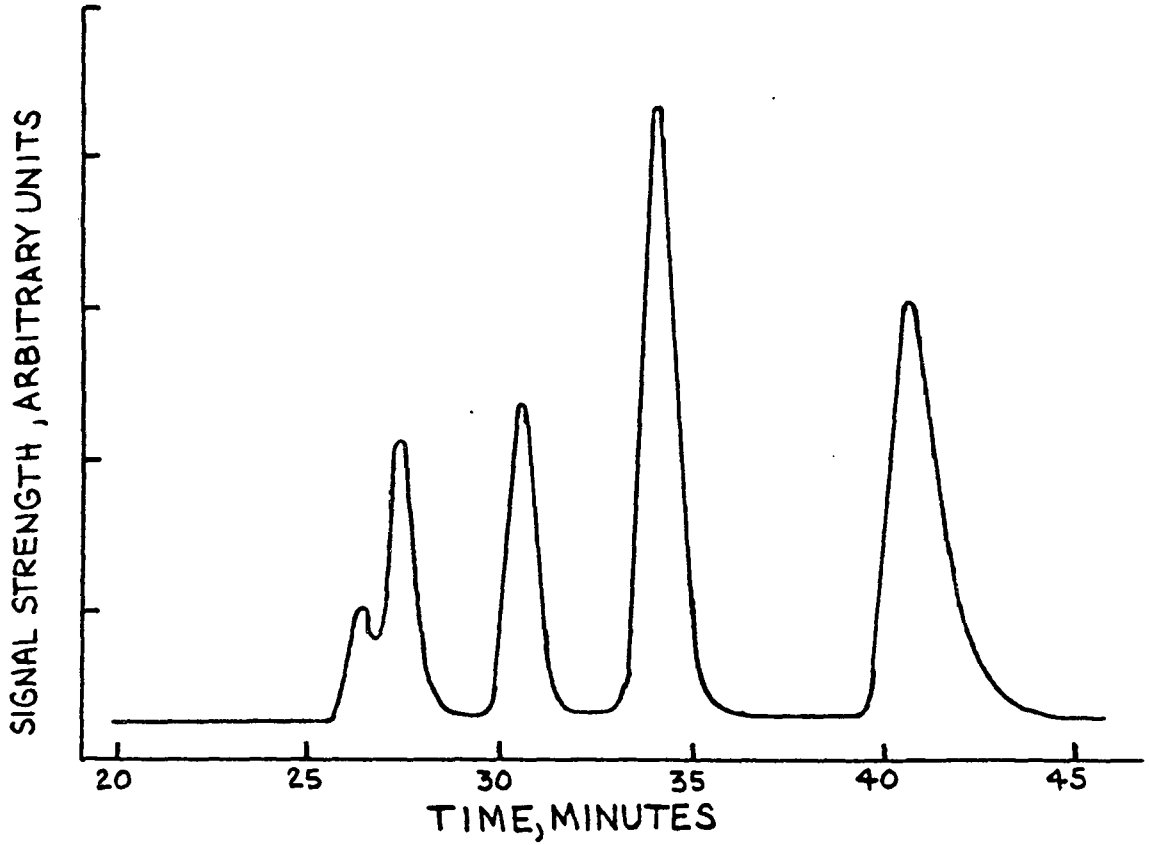


Figure A-F-2. Chromatogram of Acridine Reaction Sample (Run 1041-10) on 17' X 1/8" SS Apiezon L (2% KOH): 200°C, 25 cc/min.

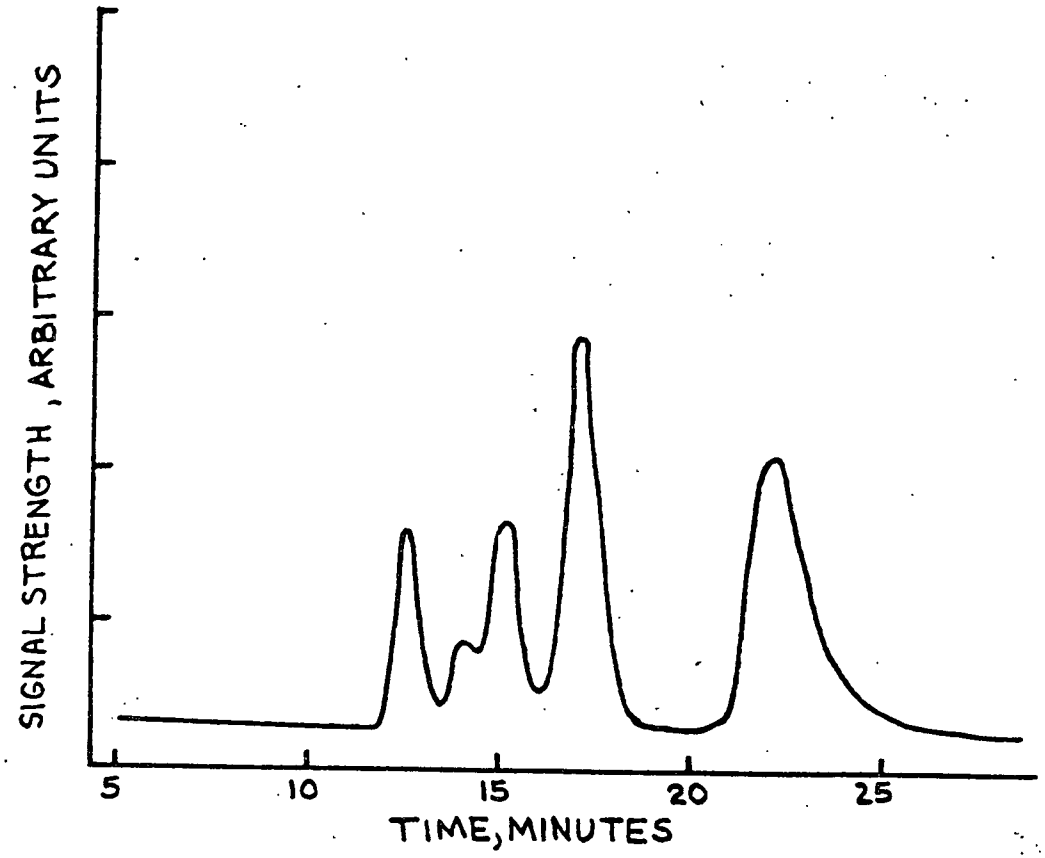


Figure A-F-3. Chromatogram of Acridine Reaction Sample (Run 1041-10) on 6' X 1/8" Chromosorb 103: 250°C, 30 cc/min.

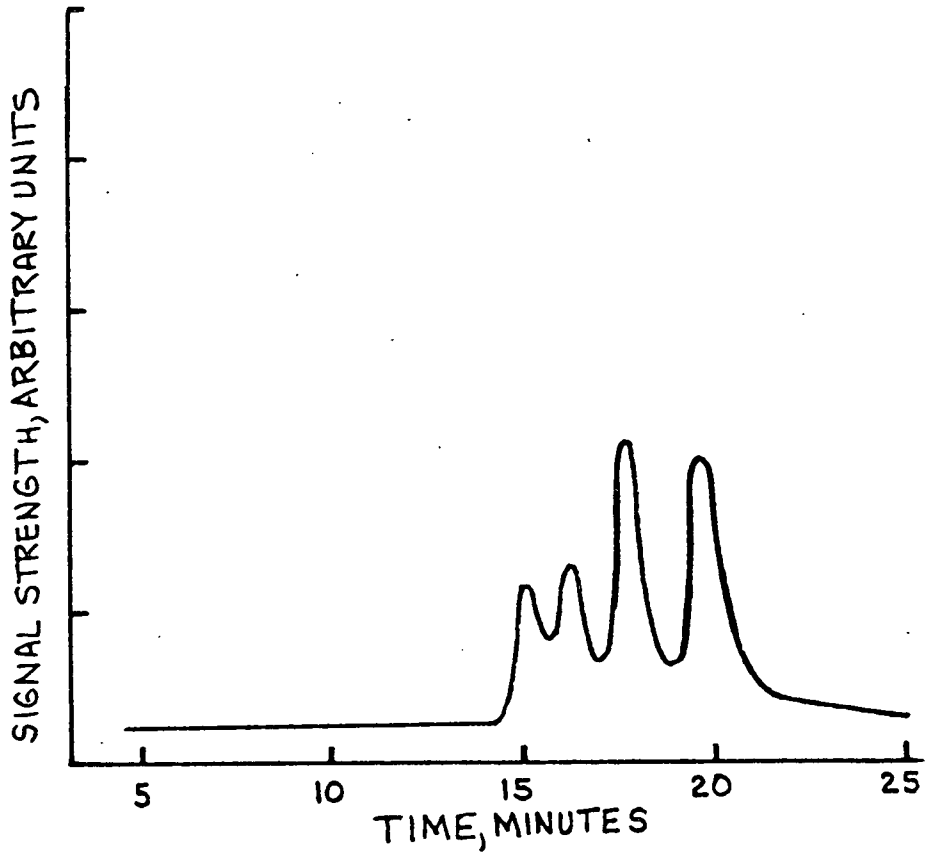


Figure A-F-4. Chromatogram of Acridine Reaction Sample (Run 1041-10) on 6' X 1/8" SS UC-W98: 160°C, 30 cc/min.

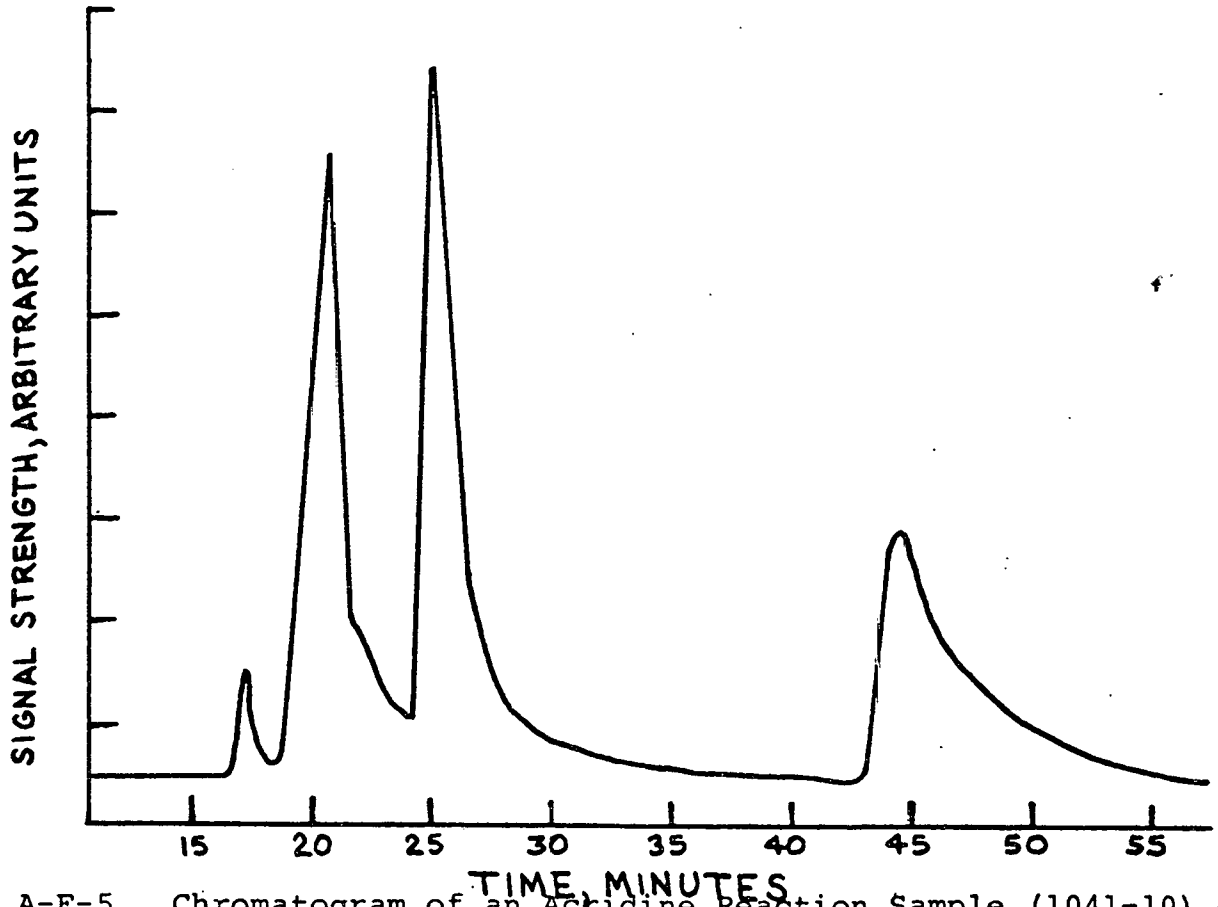


Figure A-F-5. Chromatogram of an Acridine Reaction Sample (1041-10) on 10' X 1/8" SS Carbowax 20M: 200°C, 21 cc/min.

have no severe tailing. Next, the compound retention times should not be excessively long, which was defined as greater than 45 minutes to 1 hour. Next, the temperature required to meet the above constraints should be at least 25°C lower than stationary phase thermal stability limit as suggested by the manufacturers. Finally, the nitrogen-specific detector is very sensitive to flowrate, and the flowrate required for the above constraints should not be so high as to significantly decrease the detector's response. Also, it was recognized that a stainless steel column could contribute to the various problems stated above, especially resolution and tailing; however, the supply of glass columns was not sufficient to investigate every stationary phase using glass.

APPENDIX G

EXTRACTION PROCEDURES

The following is a detailed procedure for the extraction of nitrogen-containing reaction products of acridine from white oil.

1. Extract nitrogen-containing compounds from white oil using 3-300 cc washings with 0.1M HCl.
2. Wash HCl solution with 3-100 cc portions of ether.
3. Neutralize HCl solution with 0.1M NaOH to a pH of 13. Solution should become cloudly.
4. Cool neutralized solution in ice bath.
5. Extract nitrogen compounds from neutralized solution using 3-100 cc portions of ether.
6. Wash ether solution with 100 cc of saturated NaCl solution.
7. Dy ether solution over anhydrous magnesium sulfate.
8. Filter ether solution.

9. Strip ether under reduced pressure and ambient temperature.

10. Run white oil chromatogram to make sure all nitrogen-containing compounds were extracted. (Note: No nitrogen-containing compounds were ever found in the white oil after extraction).

APPENDIX H

MASS SPECTRAL PROCEDURES AND PROBLEMS

A. Procedure

1. Predetermine gas chromatographic conditions.
2. Run sample on chromatograph-mass spectrometer system.
3. As soon as a compound peak passes through the gas chromatograph thermal conductivity detector (monitored visually on the mass spectrometer oscilloscope for appearance of fragmentation pattern).
4. Monitor the total ionization until it is maximum.
5. Record spectrum with computer software.

In most cases 10 scans were taken and averaged.

B. Discussion

1. Well-resolved compounds yielded good mass spectra.
2. For fused peaks spectra were taken over the entire area in question and then sub-

tracted from each other to yield reasonably good mass spectra if the peaks were in about the same concentration.

3. Trace amounts of compounds before or after a compound in large concentration could not be determined by mass spec.

4. Gas chromatographic preparatory work was done to isolate various sections of the extract so that these sections could be chromatographed at various conditions to optimize resolution.

5. Mass spectral structure assignments were made using standard literature fragmentation patterns as models. A published spectrum was available for acridine. When original compounds were available (acridine and sym-octahydroacridine), their spectra were obtained using the mass spec direct introduction probe.

C. Limitations

1. Mass spectroscopy yields information about molecular weights and compound structures; however, isomers have to be confirmed

by other means.

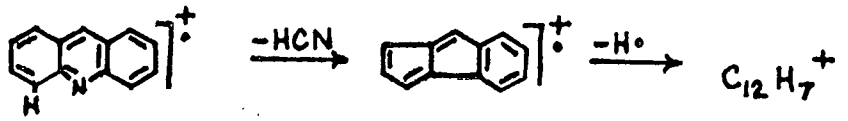
2. If the structures of two compounds are very similar, fused peaks yielded molecular weight information.

3. Many compounds do not give a molecular ion and lowering ionization voltage to retrieve this information was not always successful.

APPENDIX I

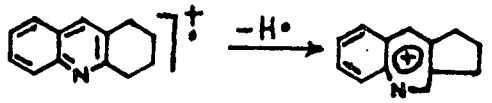
MASS SPECTRAL FRAGMENTATION PATTERNS FOR ACRIDINE NITROGEN-CONTAINING REACTION PRODUCTS

ACRIDINE

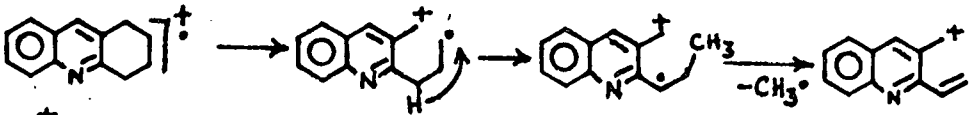


M^+ m/e 179 m/e 152 m/e 151

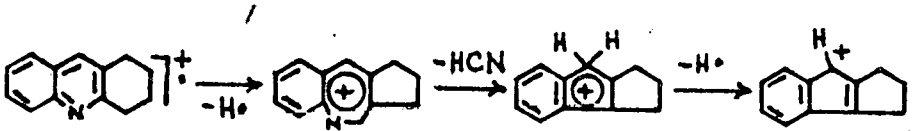
1,2,3,4- TETRAHYDROACRIDINE



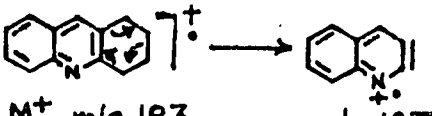
M^+ m/e 183 m/e 182



M^+ m/e 183 m/e 183 m/e 183 m/e 168



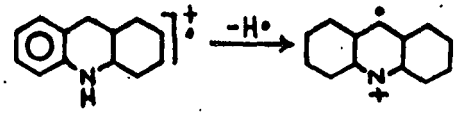
M^+ m/e 183 m/e 182 m/e 155 m/e 154



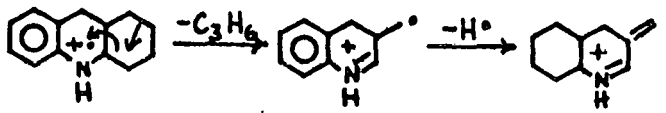
M^+ m/e 183 m/e 127

m/e 179,180,181 ACCOUNT FOR THERMAL DEHYDROGENATION

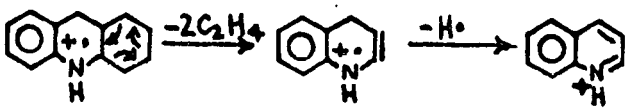
1,2,3,4,9,10,13,14-OCTAHYDROACRIDINE



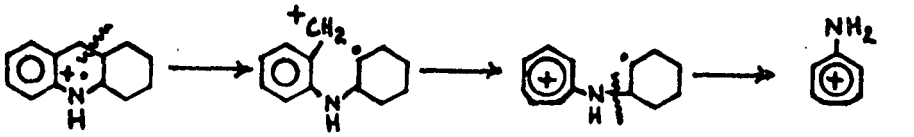
M^+ m/e 187 m/e 186



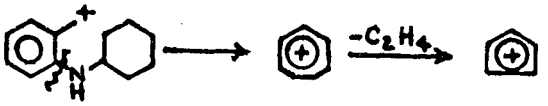
m/e 187 m/e 145 m/e 144



m/e 187 m/e 131 m/e 130



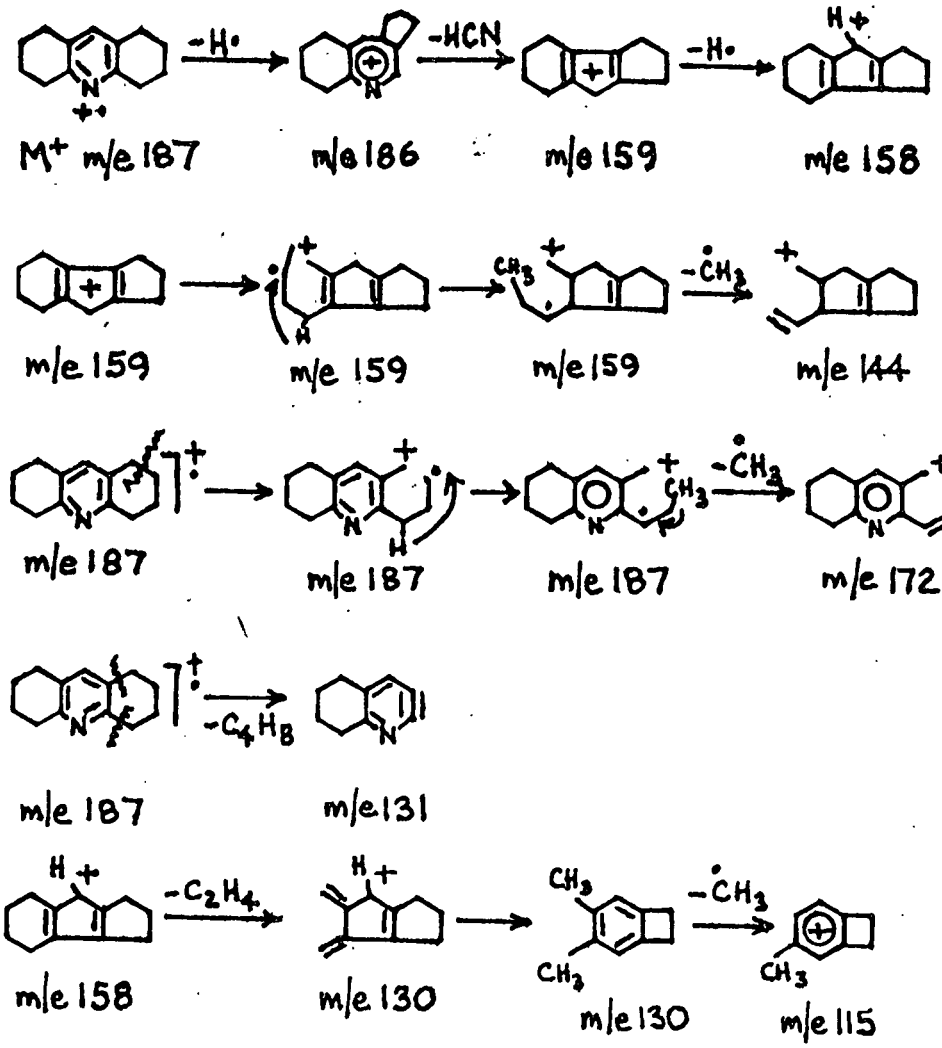
m/e 187 m/e 187 m/e 187 m/e 106



m/e 187 m/e 91 m/e 65

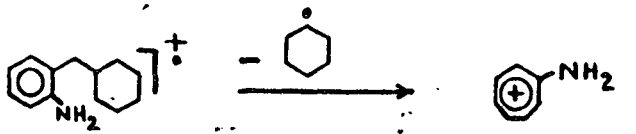
ANILINE TYPE STRUCTURES UNDERGO α CLEAVAGE OF SIDE CHAIN AS DOMINANT PROCESS YIELDING THE AMINOTROPYLIUM ION AND ALSO FRAGMENTATION OF THE AROMATIC NITROGEN BOND

1,2,3,4,5,6,7,8-OCTAHYDROACRIDINE



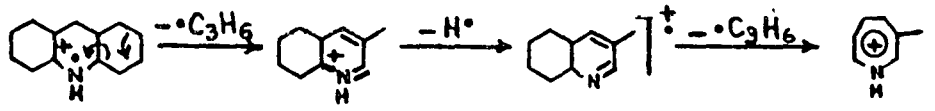
PYRIDINE TYPE STRUCTURES LOSE HYDROGEN RADICAL TO FORM AN AZATROPYLIUM ION. IN SUBSTITUTED PYRIDINES β CLEAVAGE IS IMPORTANT. NO α CLEAVAGE CAN OCCUR.

o-(METHYLENECYCLOHEXYL)ANILINE



M^+ m/e 189 m/e 106

PER-HYDROACRIDINE

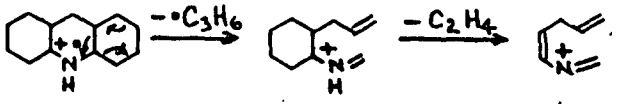


M^+ m/e 193 m/e 151 m/e 150 m/e 108

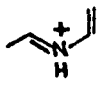
-HCN

OR

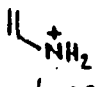
m/e 81



M^+ m/e 193 m/e 151 m/e 94



m/e 56



m/e 43

COMPOUND 1

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
17.3	2004	11.70	1.12
17.3	588	3.43	0.33
25.9	1758	10.26	0.98
25.9	3380	19.73	1.89
27.0	8813	51.45	4.93
28.0	17130	100.00	9.59
29.1	4390	25.63	2.46
30.1	6177	36.06	3.46
32.0	10848	63.33	6.07
35.9	3942	23.01	2.21
[illegible]	6385	37.27	3.57
[illegible]	3026	17.66	1.69
[illegible]	16137	94.20	9.03
[illegible]	3453	20.16	1.93
[illegible]	5917	34.54	3.31
[illegible]	829	4.84	0.46
[illegible]	1925	11.24	1.08
[illegible]	324	1.89	0.18
[illegible]	2194	13.81	1.23
[illegible]	2932	17.12	1.64
[illegible]	6979	40.74	3.91
[illegible]	[illegible]	[illegible]	3.29
[illegible]	1696	9.90	0.95
[illegible]	7345	42.88	4.11
[illegible]	3447	20.12	1.93
[illegible]	850	4.96	0.48
[illegible]	2304	13.45	1.29
[illegible]	[illegible]	[illegible]	1.01
[illegible]	3391	19.80	1.90
[illegible]	3657	21.35	2.05
[illegible]	3546	20.70	1.98
[illegible]	[illegible]	10.34	0.93
[illegible]	[illegible]	10.50	1.01
[illegible]	[illegible]	[illegible]	9.45
[illegible]	4454	26.00	2.49
[illegible]	3352	19.57	1.88
[illegible]	[illegible]	[illegible]	1.72
[illegible]	3575	[illegible]	2.00

COMPOUND 2

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
17.3	1224	7.26	2.22
27.0	4234	25.12	7.66
28.0	16856	100.00	30.51
32.0	9187	54.50	16.63
35.9	349	2.07	0.63
38.9	2288	13.57	4.14
39.9	637	3.78	1.15
40.9	4526	26.85	8.19
55.0	2514	14.91	4.55
57.0	2129	12.63	3.85
130.1	6119	36.30	11.08
150.1	5184	30.75	9.38

COMPOUND 3

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
12.4	3562		
17.4	586	21.06	8.46
27.0	1347	3.45	1.39
28.0	16813	7.36	3.09
32.0	9198	100.00	40.19
35.9	2027	47.94	19.27
40.9	4239	11.98	4.62
55.0	1444	25.08	10.07
56.0	1290	8.54	3.43
57.0	973	7.53	3.07
67.1	1341	5.16	2.07
106.1	356	7.93	3.13
		2.10	0.65

COMPOUND 4

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
25.9	1319	7.81	1.91
27.0	2586	15.33	3.74
28.0	16868	100.00	24.42
29.1	1761	10.44	2.55
32.0	7481	44.41	10.85
35.0	2275	13.49	3.29
39.9	2714	16.09	3.93
40.9	6711	39.79	9.72
42.8	1735	10.29	2.51
55.0	901	5.34	1.30
65.0	904	5.36	1.31
77.0	1223	7.25	1.77
91.0	350	2.07	0.51
91.0	370	2.19	0.54
119.0	1635	9.69	2.44
147.0	13314	78.93	19.28
148.0	1379	8.18	2.00
150.1	4070	24.13	5.89
150.2	1407	8.34	2.04

COMPOUND 5

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
27.1	1400	8.23	2.55
28.1	17003	100.00	31.00
29.2	1192	7.01	2.17
30.2	3005	17.67	5.48
32.1	6657	39.15	12.14
35.1	4231	24.88	7.72
39.1	1052	6.19	1.92
41.1	4224	24.84	7.70
43.1	260	1.53	0.47
67.4	851	5.00	1.55
153.0	13643	80.24	24.88
154.0	1323	7.78	2.41

COMPOUND 6

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
28.0	1254	7.52	2.48
29.1	575	3.49	1.13
30.1	754	4.48	1.48
41.1	4769	28.36	9.34
42.0	255	1.52	0.50
43.1	514	3.06	1.01
53.1	98	0.58	0.19
54.1	334	1.99	0.65
55.1	1874	11.14	3.67
56.1	1306	7.77	2.56
67.1	1856	11.04	3.63
69.1	320	1.90	0.63
81.1	2327	13.84	4.56
82.1	757	4.50	1.48
95.0	460	2.77	0.91
136.1	575	3.41	1.09
151.0	16815	100.00	32.93
151.9	4306	25.59	8.43
152.9	1996	11.80	3.91
153.9	9051	53.82	17.72
154.8	876	5.21	1.72

COMPOUND 7 (Per Hydroacridine)

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
27.0	674	4.05	0.88
28.1	1767	10.62	2.30
29.1	1633	9.81	2.13
30.1	783	4.70	1.02
75.0	2158	12.97	2.81
39.0	1449	8.71	1.89
41.1	6598	39.65	8.59
43.1	261	1.57	0.34
47.0	5029	30.22	6.54
49.0	2643	15.88	3.44
53.1	539	3.24	0.70
54.1	1184	7.11	1.54
55.1	1657	9.96	2.16
55.1	1142	[illegible]	1.49
67.1	1707	10.26	2.22
81.1	465	2.79	[illegible]
[illegible]	[illegible]	[illegible]	1.87
84.0	[illegible]	[illegible]	[illegible]
85.0	7718	[illegible]	10.04
[illegible]	452	2.72	0.59
150.0	16542	100.00	21.66
151.1	4117	24.71	5.35
192.0	1138	6.84	1.48
193.0	2490	14.90	[illegible]

COMPOUND 8

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
18.0	62	0.40	0.03
18.0	1403	9.08	0.74
23.9	728	4.71	0.38
25.0	2535	16.40	1.33
26.0	15141	97.94	7.97
27.1	13756	88.98	7.24
28.1	15489	100.00	8.14
29.1	6077	39.31	3.20
30.1	2222	14.37	1.17
31.0	1606	10.39	0.85
36.0	2369	15.32	1.25
38.0	1905	12.34	1.05
39.0	11653	75.41	6.14
40.1	4405	28.49	2.32
41.1	11073	71.63	5.83
43.1	1637	10.59	0.86
50.1	2752	17.87	1.45
51.1	7019	45.40	3.70
52.1	2180	14.10	1.15
53.1	4041	26.14	2.13
55.1	4765	30.82	2.51
57.1	1723	11.18	0.91
65.1	3471	22.45	1.83
77.1	5769	37.32	3.04
78.1	4359	28.20	2.30
79.1	2109	13.64	1.11
91.1	2293	14.83	1.21
93.1	1138	7.36	0.60
95.1	1295	8.38	0.68
106.1	789	5.10	0.41
117.1	984	6.37	0.52
121.0	1322	8.55	0.70
130.0	2138	13.83	1.13
141.0	549	3.55	0.29
142.0	653	4.22	0.34
143.0	3077	19.90	1.62
144.1	2293	14.83	1.21
150.1	3392	21.94	1.79
156.0	760	4.92	0.40
164.1	843	5.45	0.44
167.0	836	5.41	0.44
170.0	3187	20.62	1.68
171.0	2927	18.93	1.54
172.0	14716	95.13	7.76
173.0	2772	17.93	1.46
186.0	8700	56.23	4.58
187.0	3900	25.22	2.05

COMPOUND 9

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
15.3	2505	14.55	0.56
25.0	2763	16.05	0.62
26.0	16479	95.70	3.71
27.0	16797	97.55	3.70
[illegible]	17219	100.00	3.88
[illegible]	16261	94.44	3.66
[illegible]	4668	27.11	1.05
[illegible]	821	4.77	0.18
[illegible]	2715	15.77	0.61
[illegible]	4419	25.66	1.00
[illegible]	16810	97.62	3.79
[illegible]	10322	59.95	2.33
41.0	[illegible]	98.54	[illegible]
42.0	5219	30.31	1.18
[illegible]	[illegible]	73.72	[illegible]
[illegible]	[illegible]	4.41	0.17
[illegible]	4495	26.11	1.01
51.1	7552	43.86	1.70
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	2.00
[illegible]	5218	[illegible]	[illegible]
[illegible]	5731	[illegible]	[illegible]
[illegible]	6633	30.52	1.49
[illegible]	[illegible]	8.40	[illegible]
[illegible]	2454	14.25	0.55
[illegible]	1697	9.90	0.38
[illegible]	7354	42.77	1.66
[illegible]	4172	23.94	0.93
[illegible]	11245	65.31	2.53
[illegible]	2280	13.24	0.51
[illegible]	3141	12.43	0.48
[illegible]	1160	6.74	0.26
[illegible]	9159	53.19	[illegible]
[illegible]	5003	[illegible]	1.13
[illegible]	[illegible]	52.68	2.04
[illegible]	[illegible]	34.84	1.35
[illegible]	3446	20.01	0.78
[illegible]	2802	16.27	0.63
[illegible]	12965	75.29	2.92
[illegible]	770	4.52	0.10
91.1	5247	30.47	1.19
94.1	2428	14.10	0.55
[illegible]	3364	19.54	0.76
[illegible]	1135	6.54	0.27
[illegible]	3365	19.54	0.76
[illegible]	2049	11.90	0.46
105.0	3109	18.06	0.70
115.0	3222	[illegible]	0.73
117.0	5941	34.50	1.34
118.0	5056	29.35	1.14
119.0	3848	22.35	0.87
120.0	2510	14.58	0.57
130.0	6957	40.40	1.57
171.0	6784	39.40	1.53
132.0	3715	21.57	0.84
134.0	408	2.37	0.09
[illegible]	3253	18.89	0.73
[illegible]	[illegible]	[illegible]	0.81
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	10.47	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	21.44	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0.54
[illegible]	5825	[illegible]	[illegible]
[illegible]	[illegible]	1.09	0.04
[illegible]	16155	93.82	[illegible]
[illegible]	419	2.42	0.09
[illegible]	[illegible]	3.47	0.13
197.0	9917	[illegible]	2.01

COMPOUND 10

MASS	INTENSITY	% BASE PEAK	% TOTAL IONIZATION
10.5	[illegible]	5.00	0.50
15.0	[illegible]	[illegible]	2.10
18.5	[illegible]	3.11	[illegible]
24.0	[illegible]	[illegible]	0.30
25.0	[illegible]	[illegible]	2.16
26.0	15613	100.00	8.63
27.0	[illegible]	[illegible]	6.04
28.0	14327	91.76	7.92
29.0	5492	[illegible]	3.04
30.0	[illegible]	3.37	0.29
36.0	2960	19.01	1.64
37.0	1491	9.55	0.82
38.0	3605	23.09	1.99
39.0	12317	78.89	6.81
40.0	4143	26.54	2.29
41.0	14305	91.62	7.91
42.0	4359	27.91	2.41
43.0	3350	21.46	1.05
50.0	4165	26.68	2.30
51.0	4594	29.42	2.54
52.0	[illegible]	[illegible]	1.40
53.0	2020	[illegible]	1.57
54.0	1617	14.55	0.91
55.0	4870	30.99	2.68
56.0	1371	8.78	0.76
62.0	179	1.15	0.09
63.0	2299	14.72	1.27
65.0	2301	15.29	1.32
66.0	712	4.56	0.39
67.0	4446	28.48	2.46
68.0	691	4.45	0.39
76.0	105	0.68	0.06
77.0	5071	32.49	2.80
79.0	3977	25.47	2.20
81.0	597	3.92	0.33
90.0	421	2.76	0.23
91.0	2482	15.90	1.37
95.0	1377	8.82	0.76
106.0	622	3.90	0.34
115.0	1400	9.02	0.78
116.0	[illegible]	5.06	0.44
117.0	566	3.63	0.31
130.0	1422	9.11	0.79
136.0	664	4.25	0.37
144.0	665	4.26	0.37
150.0	6324	40.50	3.50
154.0	156	1.00	0.00
156.0	[illegible]	1.47	0.13
159.0	271	1.74	0.15
164.0	137	0.88	0.07
167.0	[illegible]	5.71	0.49
170.0	[illegible]	[illegible]	0.20
171.0	[illegible]	[illegible]	0.70
172.0	[illegible]	11.74	3.06
185.0	[illegible]	[illegible]	0.46
186.0	1141	7.31	0.63
187.0	[illegible]	[illegible]	1.07

COMPOUND 11 (o-(methylenecyclohexane)aniline

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
15.3	3497	20.36	1.21
25.0	4029	28.12	1.67
26.0	16717	97.35	5.78
27.1	16850	98.12	5.82
28.1	15914	92.67	5.50
29.1	4171	24.29	1.44
30.1	1592	9.27	0.55
36.0	3762	21.91	1.30
37.0	3246	18.90	1.12
38.0	5955	34.10	2.02
39.0	17120	99.70	5.92
40.0	5416	31.54	1.87
41.0	16915	98.50	5.85
42.1	6754	39.33	2.34
43.1	2276	13.25	0.79
50.0	5172	30.12	1.79
51.0	6201	36.11	2.14
52.1	5503	32.05	1.90
53.1	8056	46.93	2.85
54.1	8228	47.89	2.84
55.1	4830	28.13	1.67
56.1	2214	12.89	0.77
63.1	4337	25.26	1.50
64.1	1197	6.97	0.41
65.1	3324	19.36	1.15
66.1	2223	12.95	0.77
67.1	12914	75.20	4.46
77.0	2951	17.19	1.02
78.1	6201	36.11	2.14
79.1	11308	65.85	3.91
80.1	6132	35.71	2.12
90.1	1589	9.25	0.55
91.1	309	1.79	0.11
92.1	2071	12.06	0.72
93.1	3214	18.72	1.11
94.1	2109	12.28	0.73
95.0	2802	16.32	0.97
96.0	518	3.02	0.18
97.1	961	5.60	0.33
98.0	2290	13.34	0.79
104.0	2532	14.74	0.88
106.0	17172	100.00	5.95
107.0	16713	97.33	5.78
115.0	1660	9.67	0.57
130.0	3115	18.14	1.08
143.9	600	3.84	0.21
168.9	13261	77.22	4.59

COMPOUND 12 (Sym-octahydroacridine)

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
25.9	1157	29.69	4.10
27.0	1105	28.11	3.88
28.0	2320	59.02	8.14
29.0	1270	32.31	4.46
41.1	1616	41.11	5.67
42.1	1148	29.09	4.00
51.0	739	18.80	2.59
52.0	581	14.78	2.04
53.0	439	11.17	1.54
54.0	546	13.89	1.92
65.0	714	18.16	2.51
66.0	552	14.04	1.94
77.0	253	6.44	0.89
78.0	624	15.87	2.19
79.0	769	19.56	2.70
107.0	466	11.85	1.64
108.0	355	9.49	0.89
117.0	815	20.73	2.86
118.0	554	14.01	1.95
119.0	209	5.31	0.05
130.0	431	10.96	1.51
131.0	403	10.25	1.41
144.1	435	11.09	1.53
145.0	410	10.43	1.44
156.0	915	23.30	3.21
157.0	432	10.99	1.52
183.1	1275	32.45	4.48
184.1	553	14.61	2.09
185.0	386	9.82	1.35
186.0	2634	66.53	9.45
187.1	3931	100.00	13.80

COMPOUND 13 (1,2,3,4,9,10,13,14-octahydroacridine)

MASS	INTENSITY	% BASE PEAK	% TOTAL IONIZATION
29.0	[illegible]	[illegible]	6.37
37.0	[illegible]	[illegible]	0.70
38.0	[illegible]	[illegible]	0.07
[illegible]	[illegible]	[illegible]	2.84
39.0	[illegible]	[illegible]	0.29
39.1	11640	[illegible]	10.22
40.0	[illegible]	[illegible]	1.59
41.1	12171	100.00	10.62
42.1	[illegible]	[illegible]	2.52
43.0	[illegible]	[illegible]	0.42
50.0	4652	38.17	4.05
51.0	4831	35.77	4.22
52.0	2131	17.51	1.86
53.0	1699	13.60	1.47
54.0	1181	9.70	1.03
55.0	1495	12.28	1.30
56.0	822	6.75	0.72
62.0	1112	9.14	0.97
63.0	3385	27.81	2.95
64.0	763	6.27	0.67
65.0	1944	15.97	1.70
66.0	164	1.35	0.14
67.0	281	2.31	0.25
74.0	887	7.29	0.77
75.0	1605	13.19	1.40
76.0	835	6.86	0.73
77.0	4363	35.85	3.81
78.0	[illegible]	[illegible]	1.31
79.0	859	7.06	0.75
83.0	1698	[illegible]	1.40
90.0	1951	16.03	1.70
91.1	1171	9.62	1.02
102.0	528	4.34	0.45
103.0	655	5.38	0.57
104.0	961	7.90	0.84
106.0	936	7.69	0.82
115.0	2441	20.06	2.13
116.0	709	5.83	0.62
117.0	1741	14.30	1.52
119.0	1418	11.65	1.24
120.0	1541	12.66	1.34
130.0	9832	80.78	8.58
131.0	2292	18.83	2.00
142.0	409	3.36	0.36
143.0	1465	12.04	1.28
144.0	5065	41.62	4.42
145.0	493	4.05	0.43
154.0	511	4.20	0.45
155.0	158	[illegible]	0.14
156.0	803	6.60	0.70
183.0	217	1.78	0.19
186.1	[illegible]	11.50	1.22
187.1	[illegible]	[illegible]	1.03

COMPOUND 14 (1,2,3,4-tetrahydroacridine)

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
25.9	1881	25.03	3.79
26.9	7269	100.00	14.65
27.9	3354	45.14	6.70
29.0	1430	19.67	2.88
30.0	673	9.26	1.36
37.0	421	5.79	0.85
38.0	1570	21.60	3.16
39.0	6133	84.37	12.36
40.0	782	10.76	1.58
41.0	2304	31.70	4.64
42.1	900	12.38	1.81
50.0	2418	33.68	4.93
51.0	3413	46.95	6.88
52.0	506	6.96	1.02
53.0	749	10.30	1.51
61.0	332	4.57	0.67
62.0	681	9.37	1.37
63.0	1745	24.01	3.52
64.0	627	8.63	1.26
65.0	433	5.96	0.87
74.0	1631	22.44	3.29
75.0	1580	21.74	3.18
76.0	781	10.74	1.57
77.0	331	4.55	0.67
78.0	283	3.90	0.56
87.0	656	9.05	1.32
88.0	466	6.41	0.94
89.0	127	1.75	0.26
100.0	74	1.02	0.15
101.0	1025	14.10	2.07
102.1	140	1.93	0.28
111.0	684	9.41	1.38
112.0	716	9.85	1.44
113.0	1343	18.48	2.71
126.0	720	9.91	1.45
127.1	1336	18.38	2.69

COMPOUND 15 (Acridine)

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
25.9	441	10.72	3.22
25.9	500	12.16	3.65
27.0	590	14.34	4.31
28.0	1112	27.04	8.12
38.9	220	5.35	1.61
50.0	621	15.10	4.53
62.0	474	11.52	3.46
63.0	430	10.45	3.14
[illegible]	395	9.63	2.89
[illegible]	514	12.50	3.75
[illegible]	591	14.37	4.31
[illegible]	330	8.01	2.35
63.5	348	8.46	2.54
126.0	407	9.90	2.97
151.0	455	11.01	3.31
[illegible]	349	8.49	2.55
[illegible]	855	20.79	6.24
179.0	4113	100.00	30.01
180.0	937	22.78	6.84

COMPOUND 16

MASS	INTENSITY	% BASEPEAK	% TOTAL IONIZATION
27.0	1748	10.39	2.34
29.0	406	2.41	0.54
39.0	2373	14.10	3.18
41.0	2513	14.93	3.37
43.0	508	3.09	0.79
51.0	736	4.37	0.99
53.0	73	0.43	0.09
55.0	465	2.76	0.62
57.0	478	2.84	0.64
67.0	143	0.98	0.20
69.0	563	3.35	0.75
77.0	1404	8.34	1.88
79.0	201	1.19	0.27
91.0	1613	9.58	2.16
103.0	66	0.39	0.09
115.0	772	4.59	1.02
117.0	173	1.03	0.23
129.0	1804	9.62	1.80
131.0	201	1.19	0.39
143.0	321	1.91	0.43
144.0	2826	16.79	3.11
145.0	567	3.37	0.76
159.0	1177	6.99	1.58
161.0	3904	23.20	5.23
189.0	4587	27.26	6.15
191.0	4815	28.65	5.78
193.0	424	2.52	0.57
205.0	16819	100.00	22.54
206.0	16758	99.63	22.46
207.0	4981	29.60	6.67
221.0	61	0.37	0.08
222.0	864	5.13	1.29
223.0	780	4.63	1.04

APPENDIX J

CONCENTRATION PROFILES FOR ACRIDINE EXPERIMENTS

DATE OF ANALYSIS 8/7/76 RUN 1042

COMPOUND					TOTAL NITROGEN						
RET. TIME											
CONC. UNITS	$\frac{gmole}{g_{soil}} \times 10^7$	$\frac{gmole}{g_{soil}} \times 10^7$	$\frac{gmole}{g_{soil}} \times 10^7$	$\frac{gmole}{g_{soil}} \times 10^7$	$\frac{gmole}{g_{soil}} \times 10^7$						
SAMPLE #											
2	14	15	25.5	44.0	137						
30	97	31	42.5	6.9	192						
60	113	16.8	26.0	2.4	175						
120	134	11	16.9	2.5	187						
180	160	9.5	17.5	10.6	220						
240	159	9.5	16.5	2.6	207						
300	153	8.5	17.2	6.3	207						
360	124	6.3	13.1	2.1	162						

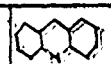
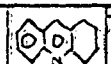
RUN CONDITIONS:

TEMPERATURE, °C 342
PRESSURE, PSIG 500
CATALYST HDS-9A
CATALYST CONC. 2g/500cc oil
CATALYST SIZE 90 μm

SOLVENT HEXADECANE
INITAL REACTANT CONC (LOADED) $2.64 \times 10^{-5} \frac{gmole}{gm}$
CS_2 CONC. (LOADED) 0.05 wt%
H_2S GAS PHASE CONC. NOT MEASURED

DATE OF ANALYSIS 10/27/76

RUN 1050

COMPOUND					TOTAL NITROGEN						
RET. TIME											
CONC. UNITS	$\frac{g\,mole}{g_{OIL}} \times 10^{7}$										
SAMPLE #											
2	19.4	19.9	31.9	17.1	273						
5	27.3	17.8	33.1	11.5	259						
10	49.3	16.5	32.4	6.6	257						
20	98.4	12.7	30.4	5.4	270						
40	164.3	8.7	17.8	1.3	290						
95	164.1	7.9	5.5	5.5	272						
120	146.8	7.3	3.0	0.2	241						
160	120.6	7.3.0	1.7	—	209						
240	8.1	55.6	3.5	6.6	88.3						
270	23.1	49.9	5.9	1.5	93.7						
300	43.0	45.7	6.0	1.4	108.						
330	39.1	35.6	2.8	—	85.7						
360	43.7	37.6	3.0	—	96.4						
450	41.3	30.8	1.4	—	93.1						
480	37.2	31.8	—	—	79.5						
544	43.0	33.4	0.9	—	96.7						
600	32.3	28.2	—	—	68.5						
630	31.1	27.4	—	—	64.8						

RUN CONDITIONS:

TEMPERATURE, °C 353
PRESSURE, PSIG 2000
CATALYST HDS-9A
CATALYST CONC. 2g/500cc oil
CATALYST SIZE 80/m

SOLVENT WHITE OIL
INITAL REACTANT CONC (LOADED) 259×10^{-7} g mole/g oil
CS_2 CONC. (LOADED) 0.05 wt%
H_2S GAS PHASE CONC. <1%