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Kenneth Eugene Johnson
Iowa State University

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KINETICS OF THE ALKYLATION AND ACYLATION OF NICKEL DIPIVALOYLMETHIDE

by

Kenneth Eugene Johnson

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Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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Ames, Iowa

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INTRODUCTION

The present knowledge of the chemistry of metal ion complexes has emanated principally from two general areas of study. The first of these includes investigations of the thermodynamic and chemical properties of metal complexes with common inorganic nucleophilic ligands. Product analysis and stereochemical analysis have been the most effective tools for the study of substitution reactions which these metal complexes undergo. A second major field of interest has centered around the use of organic compounds for complexing and separating metal ions. Most of the work in this field has resulted from efforts of analysts in their search for those reagents which have specific properties that make them valuable as reagents for quantitative separations of metal ions. Imminent among these reagents are the various oxime derivatives and ethylenediamine derivatives.

These studies have been restricted to aqueous or partially aqueous media in which the rates of reaction are too fast to be studied by conventional methods of kinetic analysis. Consequently, the study of the mechanisms of substitution reactions of metal complexes has been restricted to a very few cases.

Many metals can be converted to chelates of β-diketones which are soluble in organic solvents. The reactions of such chelates with various reagents are slow enough to be studied kinetically.

It is the purpose of this work to present a formal kinetic study of the rates of acylation and alkylation of metal complexes with enolate anions derived from β-diketones and make some attempt to clarify the mechanisms of the reactions.

Most of these studies were carried out on the nickel(II) chelate of 2,2,6,6-tetramethyl-3,5-heptadione(dipivaloylmethane, DPM). The air oxidation of this compound proved quite interesting and a report of a brief investigation of this phenomenon is included herein.

HISTORICAL

Study of the mechanisms of substitution reactions of metallic elements has been restricted to a very small number of complexes and compounds[1, 2]. This work consisted of stereochemical investigations and the study of the relative rates of reaction of metal ions and common anions with metal complexes which themselves have common anions as ligands. The reactions studied have been almost exclusively those involving exchange of metal ions or the exchange of one or more of the ligands between the various compounds. These reactions may be classified more specifically as 1) substitution reactions and 2) oxidation reduction reactions. Aqueous or partially aqueous solvents were used in most cases.

Substitution Reactions of Metal Complexes

Substitution reactions of metal coordination compounds are conveniently described as nucleophilic substitutions (S_N) and electrophilic substitutions (S_E). This terminology is synonymous with that developed by Hughes and Ingold in their description of organic reactions[3]. At least two fundamentally different pathways could be followed in substitution reactions.

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[1] H. Taube, Chem. Rev., 50, 69 (1952).

[2] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions", John Wiley and Sons, Inc., New York (1958).

[3] C. K. Ingold, "Structure and Mechanisms in Organic Compounds", Cornell University Press, Ithaca (1953).

These are labeled as dissociation (S_N1, S_E1) and displacement (S_N2, S_E2) mechanisms.

Basolo and Pearson[4] discussed several criteria for the two mechanisms. The effects of varying the sizes and charges of the central atoms and the leaving groups in octahedral complexes tend to fit the requirements of an S_N1 mechanism. On the other hand, it was found that the line of demarcation between labile and inert complexes falls at the point where the inner d-orbitals become at least singly occupied. This can be reasonably explained by an S_N2 mechanism, since the introduction of another group into the coordination sphere is greatly aided if an empty lower d-orbital is available.

Brown and Ingold[5] found that substitutions of chloro groups in cobalt(III) complexes proceed by an S_N1 mechanism. But, these could be described as an S_N2 mechanism involving the solvent as the nucleophilic reagent. A number of haloammine complexes of platinum(IV) with nucleophilic reagents showed second order behavior[6].

The existence of S_N1, S_N2, and borderline mechanisms between these two has been discovered in studies of substitution reactions of square planar complexes of platinum(II)[7].

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[4] Basolo and Pearson, op. cit., p. 895.

[5] D. D. Brown and C. K. Ingold, J. Chem. Soc., 2674 (1953).

[6] O. E. Zvyagintsev and E. F. Karandashova, Doklady Akad. Nauk S.S.S.R., 108, 447 (1956).

[7] Basolo and Pearson, op. cit., p. 172.

Calkins and Hall[8] followed the kinetics of the exchange of nickel(II) between $Ni(CN)_4^{-2}$ and amino acid complexes of nickel(II) by observing the exchange of radioactive nickel. They found the reaction to be first order in each reactant. Consequently, they postulated an S_N2 mechanism for the reaction.

Oxidation-Reduction Reactions of Metal Complexes

Redox reactions are often subdivided into electron transfer reactions and atom transfer reactions. There is evidence that the former do occur in gaseous systems. No real evidence for electron transfer in solution has been advanced.

Taube and his coworkers[9] have demonstrated the transfer of oxygen atoms in the oxidation of sulfites and nitrites with hypochlorous acid. Using chromium(II) cation as a reducing agent, they effected the transfer of a large number of univalent atoms and groups[10].

Metal Chelates of β-Diketones

Many metals have been converted to oil-soluble metal chelates of β-diketones. The physical and thermodynamic pro-

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[8] R. C. Calkins and N. F. Hall, J. Am. Chem. Soc., 80, 5028 (1958).

[9] H. Taube, Record Chem. Prog. Kresge-Hooker Sci. Lib., 17, 25 (1956).

[10] H. Taube, H. Meyers and R. L. Rich, J. Am. Chem. Soc., 75, 4118 (1953).

perties of those chelates have been thoroughly investigated. Van Uitert and Fernelius[11, 12] have studied the relative stabilities of chelates of β-diketones. The following values of log K (formation constant) for metal chelates of dibenzoylmethane were reported: Li^+ 5.95, Na^+ 4.18, K^+ 3.62, Rb^+ 3.52, Cs^+ 3.42. These values which were obtained by potentiometric measurements on several β-diketone-metal solutions, seem to indicate that the stability is a function of the size of the metal ions. A comparison of the chelating tendencies of a series of bivalent metals toward several β-diketones gave the following general order of increasing stabilities: Ba, Sr, Ca, Mg, Cd, Mn, Pb, Zn, Co, Ni, Fe, Cu, Be, Hg. A plot of log K versus electronegativity of the metals is linear except for Be.

The thermal stabilities of several metal acetylacetonates have been investigated by Charles and coworkers[13, 14]. Acetone and carbon dioxide gases were emitted as the main products when metal acetylacetonates were decomposed in the

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[11] W. Conard Fernelius and Le Grand G. Van Uitert, Acta. Chem. Scand., 8, 1726 (1954).

[12] Le Grand G. Uitert, W. Conard Fernelius and Bodie F. Douglas, J. Am. Chem. Soc., 75, 2736 (1953).

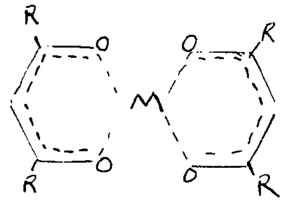
[13] Joan Von Hoene, Robert G. Charles and William M. Hickam, J. Phys. Chem., 62, 315 (1958).

[14] Robert G. Charles and Sidney Barnartt, J. Phys. Chem., 62, 257 (1958).

absence of oxygen. The following order of decreasing stabilities of several metals were based on the emission of gaseous products at 350°: Na(I), Cr(III), Al(III), Ni(II), Cu(II), Fe(II), Fe(III), Co(II), Co(III), Mn(III).

The infrared spectra of metal chelates of β-diketones are characterized by strong absorption bands in the 1550-1600 cm^{-1} and 1280-1390 cm^{-1} regions[15]. Bands in this region of the spectra have been assigned to stretching of the carbon-oxygen and carbon-carbon bonds of the chelate ring[16]. Most of these compounds also show strong absorption in the visible range.

Hammond and coworkers[17, 18] have found that the following metal chelates are easily prepared and purified.



R = phenyl-, t-butyl-

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[15] L. J. Bellamy and L. Beecher, J. Chem. Soc., 4487 (1954).

[16] B. Meeke and E. Funk, Z. Electrochem., 60, 1124 (1956).

[17] G. S. Hammond and A. W. Fort, Data from studies of metal chelates, Research notebook, U. S. Atomic Energy Commission, Ames Laboratory, Ames, Iowa (1953).

[18] G. A. Guter and G. S. Hammond, J. Am. Chem. Soc., to be published ca. 1959.

These chelates are thermally stable, light resistent, and they react relatively slowly with various organic reagents and with iodine. The method of purification and the melting points of some of these metal chelates are given in Table 1.

Table 1. Properties of metal chelates of β-diketones

Formula[a]	Method of purification[b]	Melting point
NaDPM	Sublimation	Dec. 300°
$Mg(DPM)_2$	Petroleum ether	135-137°
$Ca(DPM)_2$	Ethanol-water	232-233°
$Cu(DPM)_2$	Dimethylformamide	197-198°
$Cu(BPM)_2$	Ligroin	203°
$Cu(DBM)_2$	Toluene	296°
$Ni(DPM)_2$	Sublimation	222-225°
$Zn(DPM)_2$	Sublimation	144°
$Al(DPM)_3$	Ethanol	264-265°
$Fe(DPM)_3$	Dimethylformamide	167°
$Ho(DPM)_3$	Dimethylformamide	154-155°

[a] DPM = $[Me_3CCOCHCOCMe_3]$, DBM = $[C_6H_5COCHCOC_6H_5]$, BPM = $[C_6H_5COCHCOCMe_3]$.

[b] Recrystallization from the indicated solvents or vacuum sublimation.

A qualitative survey of several reactions which these chelates undergo in nonhydroxylic solvents has been made by Hammond and Nonhebel[19].

Reactions of chelates with acids

Metal chelates are very rapidly hydrolyzed when shaked with aqueous solutions of mineral acids or when anhydrous hydrogen halides are bubbled through the solutions. The hydrolysis products are the β-diketones from which the chelates are derived and metal salts of the acids.

Nearly all of the chelates investigated reacted immeasurably rapid with p-nitrophenol, 2, 4-dinitrophenol, and picric acid. Aluminum dipivaloylmethane (DPM) reacted slowly with picric acid. Ferric and mercuric DPM gave no observable reaction with any of the nitrophenols.

Reactions of metal chelates with iodine

All of the metal chelates except ferric DPM and aluminum DPM react with iodine in benzene. The stoichiometry of this reaction seems to be one mole of iodine per mole of chelate. The metal iodide has been isolated in 85% yield accounting for essentially all of the reacted iodine. No organic compounds were isolated.

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[19] G. S. Hammond and D. R. Nonhebel, Data from studies of metal chelates, Research notebook, U. S. Atomic Energy Commission, Ames Laboratory, Ames, Iowa (1958).

Reactions with alkyl halides

Several metal chelates have been reacted with alkyl halides, including methyl iodide and triphenylmethyl chloride. Products of both O-alkylation and C-alkylation are obtained along with the metal salts. Nickel DPM reacts with triphenylmethyl chloride to give the enol ether. The following sequence is in the decreasing order of reactivity of triphenylmethyl chloride with various metal chelates derived from DPM and BPM (benzoylpivaloylmethane): zinc, barium, potassium, nickel, and copper.

Reactions of metal chelates with acyl chlorides

Metal chelates react with acyl chlorides to give triketones, the C-acylated product, and enol esters, the O-acylated product. Any correct prediction as to where a specific acyl halide will attach the substrate seems to be a fortuitous guess. Evidence for this is shown in Table 2 which lists various reactions of metal chelates with acyl halides. The following order of decreasing reactivities was observed in the reaction of metal chelates with benzoyl chloride: potassium > barium > strontium > lanthnum > erbium > calcium > zinc > nickel > sodium > magnesium > copper > aluminum > iron.

Table 2. Reactions of metal chelates with acyl halides

Metal chelate	Acyl halide	Product
$Cu(DPM)_2$	Benzoyl chloride	Triketone
$Ni(DPM)_2$	Benzoyl chloride	Triketone
$Zn(DPM)_2$	Benzoyl chloride	Enol ester
$Zn(DPM)_2$	*p*-Nitrobenzoyl chloride	Triketone
$Ni(DPM)_2$	*p*-Nitrobenzoyl chloride	Triketone
Li(BPM)	Pivaloyl chloride	Enol ester
$Ca(DPM)_2$	Pivaloyl chloride	Triketone
$Fe(DPM)_3$	Benzoyl chloride	No reaction
$Al(DPM)_3$	Benzoyl chloride	No reaction

In an attempt to gain some insight as to the mechanism of the reaction of metal chelates with alkylating and acylating agents, Hammond and Nonhebel made qualitative comparison of substituent, solvent, and catalytic effects[20]. Table 3 shows the orders of reactivities in the reactions of the chelates with substituted benzoyl chloride in dry benzene.

The rates of reactions of metal chelates with acyl and alkyl chlorides increased with increasing polarity or basisity of the solvent. The addition of aluminum chloride or silver perchlorate accelerated the reaction.

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[20] D. R. Nonhebel, Data from studies of metal chelates, Research notebook, U. S. Atomic Energy Commission, Ames Laboratory, Ames, Iowa (1958).

Table 3. Reactions of metal chelates with substituted benzoyl chloride in dry benzene

Metal chelate	Decreasing rate of reaction
Calcium	$p\text{-NO}_2 > \text{H} > p\text{-OCH}_3$
Copper	$p\text{-NO}_2 > \text{H} > p\text{-OCH}_3$
Nickel	$p\text{-NO}_2 > \text{H} > p\text{-OCH}_3$
Zinc	$p\text{-OCH}_3 > \text{H} > p\text{-NO}_2$
Aluminum	$p\text{-OCH}_3 > \text{H} > p\text{-NO}_2$

The obvious conclusions which can be drawn from the present knowledge of the alkylation and acylation of metal chelates is that there is a significant variation in mechanisms of reactions involved.

Air Oxidation of Metal Chelates of β-Diketones

Charles and Barnartt[21] found that the reaction of metallic iron with acetylacetone is greatly accelerated by the presence of oxygen. Substantial amounts of acetic and pyruvic acids were produced as by-products. These products were also obtained from the air oxidation of Fe(II) acetylacetonate, leading Charles and Barnartt to the conclusion that Fe(II) acetylacetonate is an intermediate in the for-

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[21] Robert G. Charles and Sidney Barnartt, J. Phys. Chem., 62, 252 (1958).

mation of Fe(III) acetylacetonate.

A study of the acylation and alkylation of metal chelates in the presence and absence of oxygen might conceivably provide some hint as to the characterization of the mechanisms of these reactions.

EXPERIMENTAL[22]

Chemicals

Aluminum chloride

Anhydrous aluminum chloride (Reagent Grade, J. T. Baker Chemical Company) was used without further purification.

Ammonia

Anhydrous ammonia (The Mathison Company, Inc.) was used without further purification.

Anisole

Anisole (Reagent Grade, Matheson, Coleman, and Bell) was used without further purification.

Benzene

Thiophene free benzene (Allied Chemical and Dye Company) was distilled from sodium or phosphorus pentachloride.

Benzoyl chloride

Reagent grade benzoyl chloride (J. T. Baker Chemical Company) was used without further purification.

Chlorobenzene

Reagent grade chlorobenzene (Allied Chemical and Dye Company) was distilled through a spinning band column. The

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[22] All melting points and boiling points reported in this thesis are uncorrected.

fraction used distilled at 132°.

p-Chlorobenzoyl chloride

Reagent grade *p*-chlorobenzoyl chloride (Eastman White Label, Eastman Kodak Company) was used without further purification.

Cumene

Reagent grade cumene (Allied Chemical and Dye Company) was purified by Richard Tunder, Department of Chemistry, California Institute of Technology, Pasadena, California. The material was treated with sulfuric acid until coloration disappeared. It was then washed clean of acid and distilled through a glass bead column. The fraction boiling at 151-153° was used.

Cyclohexane

Cyclohexane (Reagent Grade, Mathison Chemical Company) was distilled from sodium metal. The boiling point was 80°.

Diethyl ether

Reagent grade diethyl ether (Matheson, Coleman, and Bell) was used without further purification.

Lithium metal

Lithium wire (Lithium Corporation of America, Inc.) was cleaned with petroleum ether.

p-Methoxybenzoyl chloride

Reagent grade *p*-methoxybenzoyl chloride (Matheson, Coleman, and Bell) was distilled through a spinning band column. The fraction boiling at 120-122° at 10 mm. was used.

Nickelous acetate tetrahydrate

Reagent grade nickelous acetate tetrahydrate (J. T. Baker Chemical Company) was used without further purification.

Nitrobenzene

Nitrobenzene (Reagent Grade, Matheson, Coleman, and Bell) was used without further purification.

p-Nitrobenzoyl chloride

Reagent grade *p*-nitrobenzoyl chloride (Matheson, Coleman, and Bell) was recrystallized from a 50% methanol-diethyl ether solution. The melting point was 72°.

Phenol

Technical grade phenol (Matheson, Coleman, and Bell) was used without further purification.

Pinacolone

Pinacolone (Technical Grade, Aldrich Chemical Company) was used without further purification.

Pivalic acid

Pivalic acid (Reagent Grade, Matheson, Coleman, and Bell) was used without further purification.

Thionyl chloride

Reagent grade thionyl chloride (Matheson, Coleman, and Bell) was used without further purification.

Toluene

Toluene (Reagent Grade, Allied Chemical and Dye Company) was refluxed and distilled from fused sodium through a Vigreaux column. The fraction boiling at 110-111° was used.

Triphenylmethyl chloride

Triphenylmethyl chloride (Eastman White Label, Eastman Kodak Company) was recrystallized from petroleum ether in the presence of acetyl chloride. The starting material was a pink-orange color. This material was dissolved in petroleum ether, to which was added a few ml. of acetyl chloride. The solution was treated with activated carbon (Norite A). White needles melting at 110-111° were obtained after filtering and cooling the solution. Triphenylmethyl chloride was also recrystallized from pure petroleum ether in a dry box.

Preparation of Dipivaloylmethane

Preparation of trimethylacetyl chloride

An ether solution of 600 g. of trimethylacetic acid and 845 g. of thionyl chloride was refluxed for 3 hours. The reaction mixture was fractionated through a spinning band column. The fraction boiling below 100° was discarded. The yield was 620 g. (88%) of pivaloyl chloride which boiled at 105-107°.

Preparation of phenyl pivalate

A three necked flask containing 500 g. of phenol, 150 g. of magnesium metal and 500 ml. of benzene was fitted with a stirrer, condenser, and addition funnel. The mixture was brought to a reflux temperature. Six hundred and twenty g. of pivaloyl chloride and 500 ml. of benzene were placed in the addition funnel and added to the refluxing mixture over a two hour period. The solution was then refluxed for a further four and one-half hours. Hydrogen chloride evolution could then no longer be detected. The solution was filtered, diluted with ether, and washed with 5% aqueous sodium hydroxide. The ether layer was dried over calcium chloride. Benzene and ether were stripped off through a Vigreaux column. The remaining product was distilled through a spinning band column. A yield of 830 g. (90%) was collected over a temperature range of 95-97° at 10-13 mm.

Preparation of lithium dipivaloylmethane

A three-necked flask fitted with stirrer, condenser, and gas inlet was immersed in an acetone-dry ice bath. About 1500 ml. of anhydrous ammonia was admitted at a rate to allow only slight reflux. Approximately 30 g. of lithium wire (1-2 inch strips) was added over a period of one hour. After adding 0.2 g. of ferric nitrate, the solution was stirred for 2½ hours. The stirring was discontinued and the acetone-dry ice bath removed. About one liter of ether was added when the mixture reached room temperature. Lithium amide was seen as a white suspension after the solution stood overnight. The mixture was refluxed for one hour to drive off any remaining ammonia.

A solution of 350 g. of pinacolone in dry ether was added over a 1½ hour period (ether refluxed slowly) to the lithium amide suspension. A solution of 350 g. of phenyl trimethylacetate and 200 ml. of dry ether was then added within one-half hour. The mixture was refluxed for 4½ hours during which time the stirring was continued vigorously. The product was poured into ice water producing a white butter-like suspension. The solid lithium dipivaloylmethane was filtered and washed with water.

Hydrolysis of lithium dipivaloylmethane

One hundred gram portions of lithium dipivaloylmethane were placed in a separatory funnel containing one liter of ether. Most of the solid remained undissolved. The suspension was shaked with 100 ml. portions of 5-10% aqueous hydrochloric acid until the solid material dissolved and the red color (traces of ferric dipivaloylmethane) disappeared.

The ether solutions from the above hydrolysis were combined. The solvent was removed by distillation through a 12 inch Vigreaux column. The remaining material was passed through a spinning band column. A 90% yield of dipivaloylmethane was obtained. The boiling point was 93° at 20 mm.

Preparation of Metal Chelates of Dipivaloylmethane

Preparation of nickel dipivaloylmethane

Dipivaloylmethane and nickelous acetate were dissolved in a 50% ethanol-water solution. The solution was shaked for 30-45 minutes. A green flocculent precipitate of nickel dipivaloylmethane dihydrate was formed. The precipitate was thoroughly washed with an ethanol-water solution and then dried under a heat lamp which dehydrated the chelate to form a pink solid. This solid was sublimed three times at 150° at 5 mm. The first sublimation was interrupted after an oil (probably dipivaloylmethane) was deposited on the condenser.

A light yellow residue (nickel acetate) remained after the nickel chelate sublimed. The nickel chelate (85% yield) melted at 222-225°.

Preparation of zinc dipivaloylmethane

The above procedure was followed for the preparation of zinc dipivaloylmethane which melted at 144°.

Preparation of copper dipivaloylmethane

Copper dipivaloylmethane was precipitated in the same manner as nickel and zinc dipivaloylmethane. The product was purified by recrystallization from dimethylformamide (melting point 197-198°).

Visible Absorption Spectra of Nickel DPM

Visible absorption spectra of nickel DPM in benzene and in cyclohexane were determined with a Beckman Model DU spectrophotometer and matched 1 cm. silica cells. A plot of percent transmittance versus wavelength gave a smooth curve with a minimum at 534 mμ. The molar extinction coefficient (ϵ, 534 m) of a 5.7×10^{-3} molar solution of nickel DPM in benzene was found to be 54. Plots of log % transmission versus concentration of nickel DPM in benzene and in cyclohexane gave good straight lines indicating that nickel DPM follows Beers Law in both solvents over a concentration range 0.01-0.001 molar.

Air Oxidation of Nickel DPM

Solutions of nickel DPM in various solvents were oxidized by allowing them to stand open to the atmosphere. These experiments were conducted by placing the solutions in Erlenmeyer flasks, stoppered and unstoppered, and observing the disappearance of the pink-violet color which is characteristic of nickel DPM. Three 10 ml. portions of a 0.01 molar solution of nickel DPM in benzene were prepared. Sample number one was left unstoppered; sample two was stoppered with an unrolled cork; the third sample was stoppered tightly with a lightly greased ground glass plug. The following times were required for the disappearance of the pink color of samples 1, 2, and 3 respectively: 12 hours, 30 hours, indefinite. Similar results were obtained when this experiment was repeated using toluene and chlorobenzene as solvents.

An attempt was made to oxidize nickel DPM in cyclohexane. The procedure followed was similar to that described with the solvents above. No disappearance of the nickel DPM color was detected even when the cyclohexane solutions were saturated with water.

Quantitative oxidation of nickel DPM

An investigation of the quantitative oxidation of nickel DPM was made. The rates and amounts of oxygen uptake were measured in the gas apparatus described by Boozer, Hammond, Hamilton, and Sen[23].

Oxidation in chlorobenzene   Five ml. of 5.6×10^{-2} molar solution of nickel DPM in chlorobenzene was placed in the gas apparatus at 70°. The volume of oxygen uptake was followed by observing the level of oil (Convoil 20) in the burettes.

Oxidation in anisole   Attempts were made to oxidize nickel DPM in anisole. Five ml. of a saturated solution was placed in the gas apparatus over oxygen. About one ml. of oxygen was absorbed over a six hour period. After 18 hours, the solution was yellow. This solution was placed in a 10 ml. flask fitted to a reflux condenser. After refluxing five minutes, the pink-violet color was observed. The yellow color reappeared when the solution was allowed to stand open to the atmosphere 24 hours. The solvent was distilled, leaving a solid which appeared to be nickel DPM (melting point 215-218°). No depression of the melting point was observed when the solid was mixed with authentic nickel DPM.

Oxidation in nitrobenzene   The procedure followed in the oxidation of nickel DPM in anisole was repeated using nitrobenzene as solvent.

Oxidation in cyclohexane   Five ml. of a 0.01 molar solution of nickel DPM in cyclohexane was placed in the gas

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[23] Charles E. Boozer, G. S. Hammond, Chester E. Hamilton, and Jyotrindia V. Sen, *J. Am. Chem. Soc.*, *77*, 3233 (1955).

apparatus. No significant amount of oxygen was absorbed within 2 hours. No color change was noticed after prolonged standing.

Initiation of cumene oxidation by nickel DPM

The oxidation of cumene was followed by using the gas apparatus described previously. A typical reaction involved 4 ml. of a 0.01 molar nickel DPM-chlorobenzene solution and 2 ml. of cumene.

Study of the products of air oxidation of nickel DPM

Ten g. of unsublimed nickel DPM was dissolved in 200 ml. of chlorobenzene. This solution was allowed to stand open to the atmosphere for three weeks. The color of the solution changed from the pink-violet color to a dark green. The solvent was evaporated, leaving a green crystalline solid which melted above 285°.

Solubility studies Solubility tests were made by shaking 50 mg. samples of the material with 3 ml. of several pure solvents. The material dissolved in the following solvents: chloroform, carbon tetrachloride, benzene, petroleum ether, and ethanol. Recrystallization could not be effected successfully in any of these. The product could be reprecipitated from ethanol by adding a few drops of water. This precipitate analyzed as follows: C, 39.28%; H, 6.21%.

Elemental analysis The product from the air oxidation in chlorobenzene was analyzed for chlorine by the procedure outlined by Shiner and Fuson[24]. No chlorine was detected.

Infrared spectra Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer. These spectra were obtained from nujol mulls and solutions of the material in carbon tetrachloride.

Gas chromatographic separation A benzene solution of the product from the air oxidation of nickel DPM was separated on a gas phase chromatographic instrument (Aerograph Model, Wilkins Instrument and Research, with a Varian Associate graphic recorder). About 1 g. of the solid was dissolved in 2 ml. of benzene. Five microliters of this solution was injected into an asphalt "B" column at 170°. The recorder was set at high speed. The gas phase chromatogram of the above solution was compared to that of a solution of pivalic acid in benzene. Peaks occured at corresponding positions on the two graphs. When equal parts of the two solutions were mixed, no new peak was observed.

Hydrolysis of oxidation product An ether solution (0.1 g. of the product of nickel DPM oxidation in 10 ml. of diethyl ether) was placed in a separatory funnel. This

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[24] R. L. Shiner and R. C. Fuson, "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., New York (1948) p. 55.

solution was shaken with five 5 ml. portions of 0.1 molar aqueous hydrochloric acid. The ether layer was dried with anhydrous calcium sulfate. When the ether was evaporated, a solid material (melting point, 25-30°) remained.

The infrared spectrum of this solid (using sodium chloride plates) was taken. This spectrum was identical to that of pivalic acid.

A gas phase chromatogram (instrument described previously) of the hydrolysis product was obtained. Five microliters of a solution of the solid in ether was put through an Apiezon "C" column at 150°. Two peaks were observed. These peaks were identical with those found when an ether solution of pivalic acid was chromatographed.

Preparation of nickel pivalate An authentic sample of nickel pivalate was prepared as follows: pivalic acid was saturated with nickel acetate at 100° in a round bottomed flask. The flask was further heated and some acetic acid distilled off. On cooling, a green precipitate formed. The precipitate analyzed as follows: C, 39.62%; H, 6.78%.

Reaction of Nickel DPM with Triphenylmethyl Chloride

About 75 ml. of cyclohexane was added to a 100 ml. round bottomed flask fitted with a reflux condenser and drying tube. Equimolar quantities (2.7 g. trityl chloride, 4.2 g. nickel DPM) were added. This solution was refluxed for four hours. A quantitative yield of nickel chloride was isolated. The organic product was not separated.

Reactions of Nickel DPM with Benzoyl Chloride

A solution of 3 g. of nickel DPM, 1 g. of benzoyl chloride, and 75 ml. of cyclohexane was placed in a 100 ml. round bottomed flask. The flask was fitted with a reflux condenser and drying tube. The solution was refluxed for $2\frac{1}{2}$ hours. A yellow precipitate was formed. The precipitate was collected, washed with cold cyclohexane, and added to 10 ml. of distilled water. Part of the precipitate dissolved in water. The remaining solid was washed with water and then dissolved in methanol. A few drops of water was added. The solid precipitated as white needles (melting point 172-173°). Anal. calcd. for $C_{18}H_{24}O_3$: C, 74.98%; H, 8.39%. Found: C, 75.40%; H, 8.31%.

An infrared spectrum of the product was taken using 0.1 mm. cells with chloroform as the solvent.

Reaction of Nickel DPM with
ρ-Methoxybenzoyl Chloride

A round bottomed flask was fitted with a reflux condenser and drying tube. A solution containing 3 g. of nickel DPM and 1.62 g. of ρ-methoxybenzoyl chloride in 75 ml. of cyclohexane was placed in the flask and refluxed. A yellow precipitate began forming immediately. Refluxing was continued until the color of nickel DPM had disappeared (4 hours). The yellow precipitate was then collected and washed with cold cyclohexane. When placed in water, part of the solid dissolved. The remaining solid was washed with water and then recrystallized in petroleum ether.

The infrared spectrum of the solid was measured using chloroform as the solvent.

Kinetics of the Reaction of Nickel DPM with Triphenylmethyl Chloride

The reactions were carried out in 100 and 200 ml. round bottomed flasks each of which has a side arm with a diameter of 1 cm. The flasks were stoppered in most cases. The side arms were fitted with rubber serum caps. The flasks were immersed in a constant temperature bath, a 12 x 12 inch beaker filled with mineral oil (Mefford Chemical Company). The oil was heated with a blade type heater which was controlled by an electronic relay (Precision Scientific Company).

A description of a typical kinetic run follows: A solution containing 1.1274 g. of triphenylmethyl chloride in cyclohexane was diluted to 50 ml. in a volumetric flask. A sample of nickel DPM weighing 0.4550 g. was placed in a second volumetric flask and diluted to 50 ml. with cyclohexane. The flasks were suspended in the oil bath for 15 minutes. The solutions were then poured into the reaction flask, flushed with nitrogen, and stoppered with a standard taper plug.

Samples were extracted through the side arm with a 5 ml. syringe fitted with a hypodermic needle. Each sample was immediately transferred to a centrifuge tube, cooled in an ice bath, and centrifuged for five minutes. The sample was then transferred to a 1 cm. silica cell which was placed in the spectrophotometer for the determination of the remaining nickel DPM.

Runs with nickel chloride added

Anhydrous nickel chloride was prepared by bubbling anhydrous hydrogen chloride through a 0.01 molar solution of nickel DPM in cyclohexane. The nickel chloride was washed several times with dry cyclohexane. This product was added to the reaction flask and the kinetic run described previously was repeated.

Runs with dipivaloylmethane added

A typical kinetic run was made with a solution which contained one ml. of dipivaloylmethane(DPM).

Catalytic effects of aluminum chloride

An attempt was made to make a cyclohexane solution of trityl chloride-aluminum chloride complex similar to those described by Brown and coworkers[25]. A solution of 0.5637 g.

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[25] H. C. Brown and F. R. Hensen, *J. Am. Chem. Soc.*, *80* 2291 (1958).

of trityl chloride (0.004 moles) was placed in the reaction flask with an equimolar amount of aluminum chloride. A stirring bar was placed in the flask to permit magnetic stirring. The solution was heated to 50° and stirred vigorously. A yellow-orange color appeared, but only part of the aluminum chloride dissolved.

Kinetics of the Reaction of Nickel DPM with Benzoyl Chloride

A stock solution of benzoyl chloride was prepared by dissolving 2.4690 g. of benzoyl chloride in cyclohexane and diluting to 50 ml.

A standard nickel DPM solution (0.24 molar) was prepared. Fifty ml. of the nickel DPM solution was placed in the reaction vessel. Ten ml. of the benzoyl chloride solution was diluted to the mark on a 50 ml. volumetric flask. After being thermally equilibrated in the bath, the solutions were mixed. Samples were extracted and analyzed as described previously for the kinetics of the triphenylmethyl (trityl) chloride-nickel DPM reaction.

The rate of benzoylation was followed in the absence of oxygen. The standard solutions of benzoyl chloride and nickel DPM were pipetted into the reaction flask. The flask was fitted with a gas inlet tube which contained a tapered stopcock. The tube was attached to a degassing apparatus. This apparatus consisted of a bulb fitted with stopcocks for a vacuum line and a nitrogen inlet. After freezing the solution in a dry ice-isopropanol mixture, the system was degassed three times. Nitrogen was admitted until the pressure inside the flask was slightly below atmospheric pressure. After the solution melted, it was placed in the constant temperature bath. The rate of reaction was followed as before.

Runs with nickel chloride added

The procedure followed for the study of the catalytic effect of nickel chloride in the trityl chloride-nickel DPM reaction was repeated for the benzoylation reaction.

Runs with DPM added

The study of the effect of DPM on the rate of benzoylation was made. The procedure described for determining the effect of DPM in the tritylation of nickel DPM was repeated.

Runs with water added

A typical rate run was made in which the cyclohexane was presaturated with water. The saturation was accomplished by shaking a cyclohexane-water mixture in a stoppered Erlenmeyer flask. The cyclohexane was pipetted from the mixture.

Catalytic effect of aluminum chloride

The aluminum chloride catalysis was investigated following the procedure outlined for the study of tritylation of nickel DPM.

Catalytic effect of the product from the oxidation of nickel DPM in benzene

The oxidation product (0.1 g.) was added to a reaction flask during a typical kinetic run.

Kinetics of the Reaction of Nickel DPM with *p*-Methoxybenzoyl Chloride

A standard solution (0.215 molar) of anisoyl chloride was prepared by dissolving 3.6715 g. in 100 ml. of cyclohexane. Ten ml. of this solution was diluted to 50 ml. This was added to 50 ml. of the nickel DPM solution, both having been preheated to the desired temperature. Samples were extracted at various intervals and analyzed. The rate of the methoxybenzoylation of nickel DPM was followed in a degassed system similar to that described for the benzoylation.

Catalysis studies

The catalytic effects of the following reagents in the methoxybenzoylation of nickel DPM were investigated: anhydrous nickel chloride, dipivaloylmethane, water, anhydrous aluminum chloride, and the product of nickel DPM oxidation.

The experimental procedures followed during these studies were identical to those described for the study of the catalytic effects of these reagents in the tritylation and benzoylation.

Kinetics of the ρ-Chlorobenzoylation of Nickel DPM

Fifty ml. of the standard nickel DPM solution were mixed with 50 ml. of a ρ-chlorobenzoyl chloride-cyclohexane solution (0.045 molar). The kinetics were followed in the presence and absence of oxygen. The procedures were similar to those previously described.

RESULTS AND DISCUSSION

Preliminary Remarks

Nickel dipivaloylmethide was used in these studies for several reasons. It is a very stable chelate which is easily sublimed in vacuo. Nickel DPM is moderately soluble in most organic solvents. Preliminary studies indicated that the moderate rates of alkylation and acylation of nickel DPM, compared to other metal chelates, are favorable for formal kinetic studies. The products obtained from alkylations and acylations of the nickel chelate are typical of those from most metal chelates.

Nickel DPM offers several possible methods of analysis. The chelate itself as well as the nickel chloride produced in the reaction have characteristic absorptions in the visible range. This, plus the ease of determination of nickel by chemical methods, made nickel DPM seem very attractive as a substrate for alkylations and acylations.

Triphenylmethyl chloride and benzoyl chloride were selected as the reagents because the products of tritylation and benzoylation are solids which were seemingly easily characterized. The desire to determine substituent effects necessitated the use of substituted benzoyl halides.

Presentation and Discussion of Data

The rates of reaction of nickel DPM with trityl chloride and with p-H, p-OCH_3, p-Cl, and p-NO_2 benzoyl chlorides were studied at three temperatures (30°, 50°, and 60°). Cyclohexane was found to be a satisfactory solvent. Since earlier investigations of the reactivity of metal chelates of -diketones[26] were made in aromatic solvents, benzene was originally chosen as the solvent in these kinetic studies. But, it was found that the color of a nickel DPM-benzene solution turned from pink-violet to green after this solution was allowed to stand open to the atmosphere. This phenomenon was originally explained as the hydration of nickel DPM to the octahedral dihydrate. The same observations were made when the experiment was repeated with dry benzene, toluene, and xylene. The fact that the rate of change of the color was fastest in very loosely stoppered flasks shows that the substance which caused this effect was an atmospheric constituent, either water or oxygen. Since the atmospherically catalyzed phenomenon did not occur when cyclohexane was used as solvent, the latter was chosen as the solvent for the kinetic studies.

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[26] G. S. Hammond and D. R. Nonhebel, Unpublished studies, Iowa State College, Ames, Iowa (1958), Present Address, G. S. Hammond, Chemistry Department, California Institute of Technology, Pasadena, California.

Air oxidation of nickel DPM

The effect of an atmospheric substituent on a benzene-nickel DPM solution was found to be an air oxidation of nickel DPM. Nickel DPM is rapidly oxidized in benzene and chlorobenzene. The uptake of oxygen by a nickel DPM-chlorobenzene solution is shown in Figure 1. There is an inhibition period which seems to be due to an impurity in nickel DPM. The inhibition period decreased with continued purification of the chelate. Unsublimed nickel DPM has a very long inhibition period.

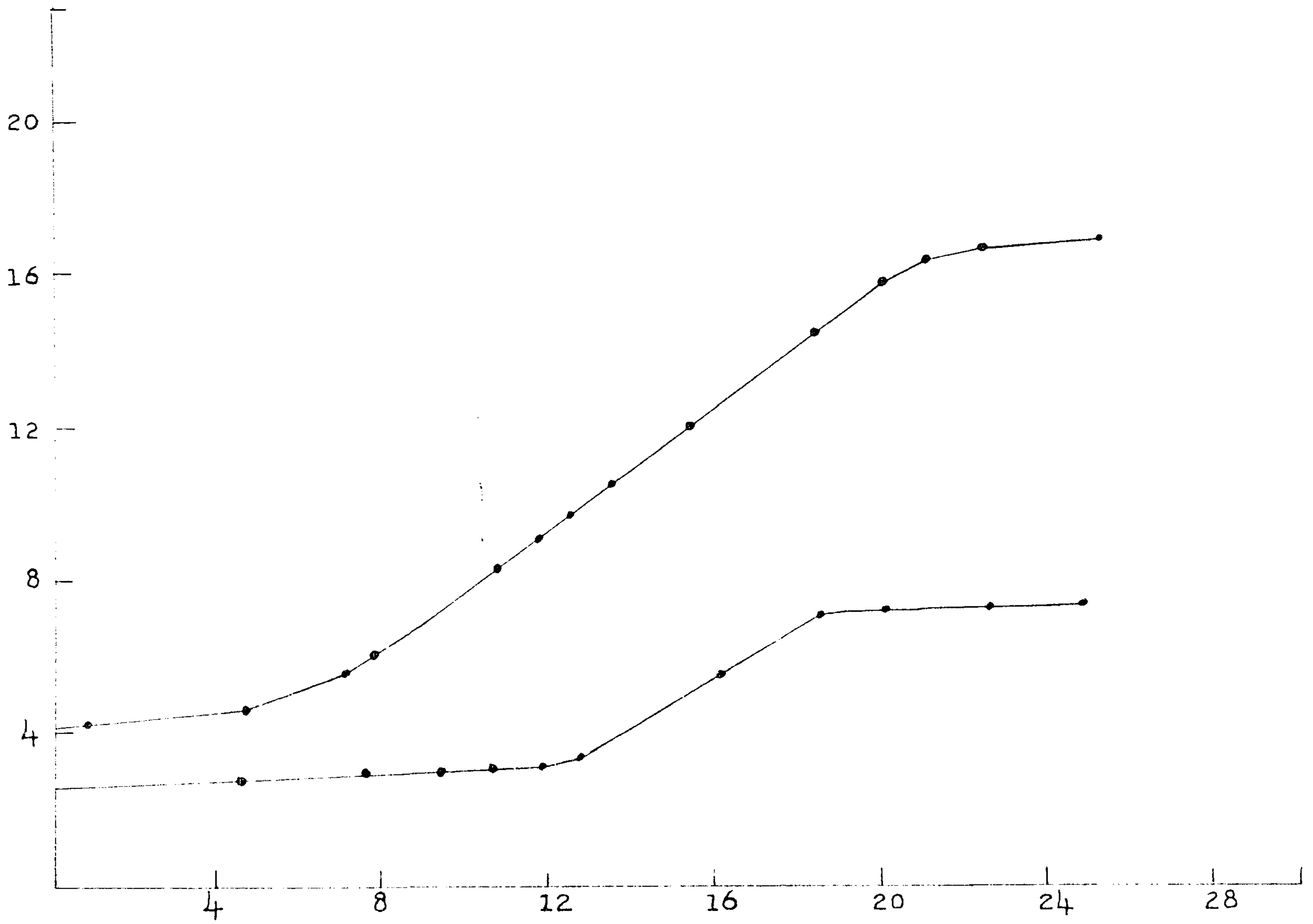
More than two moles of oxygen are absorbed per mole of nickel DPM. This uninitiated oxidation seems to take place only in various aromatic solvents.

No oxidation occurs in cyclohexane. Under the conditions of these studies anisole-nickel DPM and nitrobenzene-nickel DPM solutions undergo the color changes observed in the oxidation, but no appreciable oxygen absorption is observed. The original color of nickel DPM is regenerated when these solutions are refluxed for five minutes. After reversing this process several times, nickel DPM can be recovered. Apparently oxygen complexes or complexes of nickel DPM with these solvents are formed.

The known products of the air oxidation of nickel DPM in cyclohexane are pivalic acid, and nickel pivalate. A comparison of the vapor phase chromatogram of a benzene

Figure 1. Oxygen uptake by a DPM-chlorobenzene solution

abscissa - Time (minutes)
ordinate - Ml. of oxygen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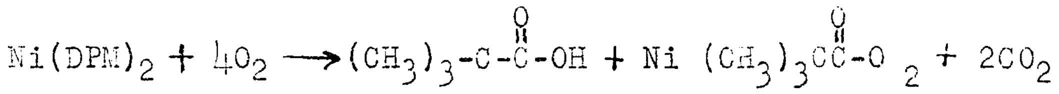
solution of the oxidation product, a pivalic acid-benzene solution, and a mixture of these is shown in Figure 2. Pivalic acid could be detected only with a very concentrated solution of the oxidation product.

About 0.1 g. of the solid product was hydrolyzed with aqueous hydrochloric acid. The only organic product found was pivalic acid. The yield of pivalic acid is much too high to have been there all the time. The vapor phase chromatogram of the hydrolysis product compared to that of authentic pivalic acid is shown in Figure 3. These results plus infrared spectra and C, H, analysis indicate that the solid product of nickel DPM oxidation is nickel pivalate dihydrate. No chlorine was detected in an elemental analysis. The oxidation of the solvent does not occur under the conditions of the reaction.

The analysis of the product of the oxidation of nickel DPM is consistent with the following stoichiometry.



$$Ni(DPM)_2 + 4O_2 \longrightarrow (CH_3)_3\text{-}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + Ni\ (CH_3)_3C\overset{O}{\overset{\|}{C}}\text{-}O\ _2 + 2CO_2$$

No evidence for the production of CO_2 was found. The small amount of pivalic acid which was isolated indicates that equimolar amounts of nickel pivalate and pivalic acid are formed.

The necessity of an aromatic solvent for the oxidation of nickel DPM seems to indicate that an intermediate is formed

Figure 2. Gas phase chromatogram of product of oxidation of nickel DPM compared to that of Authentic Pivalic Acid

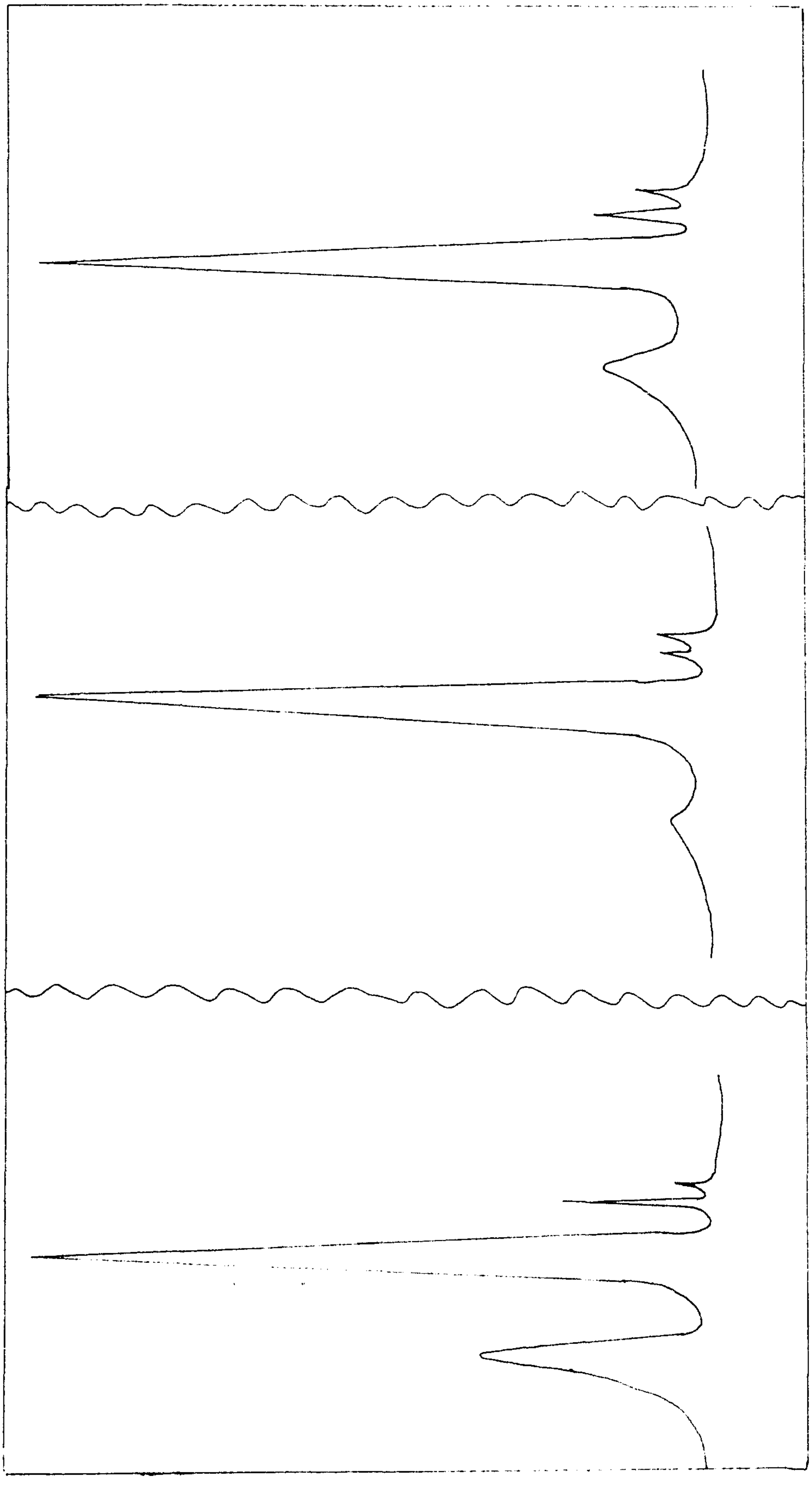
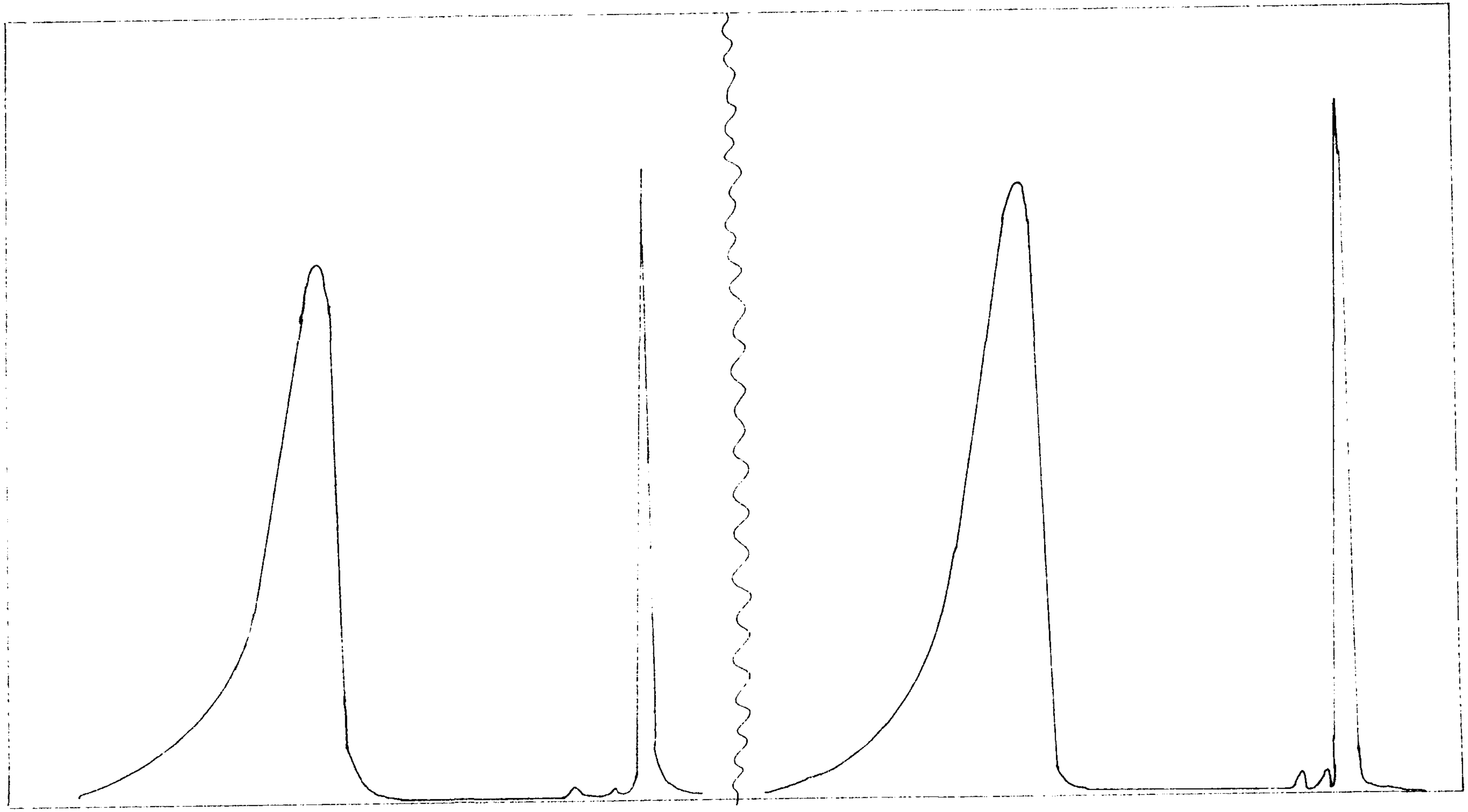


Figure 3. Gas phase chromatograms of hydrolysis product of nickel pivalate and authentic pivalic acid



which is stabilized to some extent by an electron rich system.

Initiation of cumene oxidation by nickel DPM

The initiation of the oxidation of cumene by nickel DPM is illustrated in Figure 4. After an inhibition period of four hours, cumene is oxidized at a rate similar to that when cumene is initiated with azo-bisisobutyronitrile.

Products and Stoichiometry of tritylation and acylation of nickel DPM

The organic product of the reaction of trityl chloride with nickel DPM in cyclohexane has not been rigorously identified. The spectrum of this product is compatible to that for an enol ether. The difficulty in isolating the pure material plus the isolation of large amounts of triphenylcarbinol seem to indicate that O-tritylation has occurred.

The products of acylations of nickel DPM are the triketones. The identification of these products were based primarily on their spectra and elemental analysis. Infrared spectra of the products of benzoylation and -methoxybenzoylation of nickel DPM are shown in Figure 5. The spectrum of the product of p-chlorobenzoylation is very similar to those shown.

The stoichiometry of the tritylation is two moles of trityl chloride per mole of nickel DPM. This was confirmed in several kinetic runs in which an excess of nickel DPM was

Figure 4. Initiation of cumene oxidation by $Ni(DPM)_2$

abscissa - Time (minutes)
ordinate - Ml. of oxygen

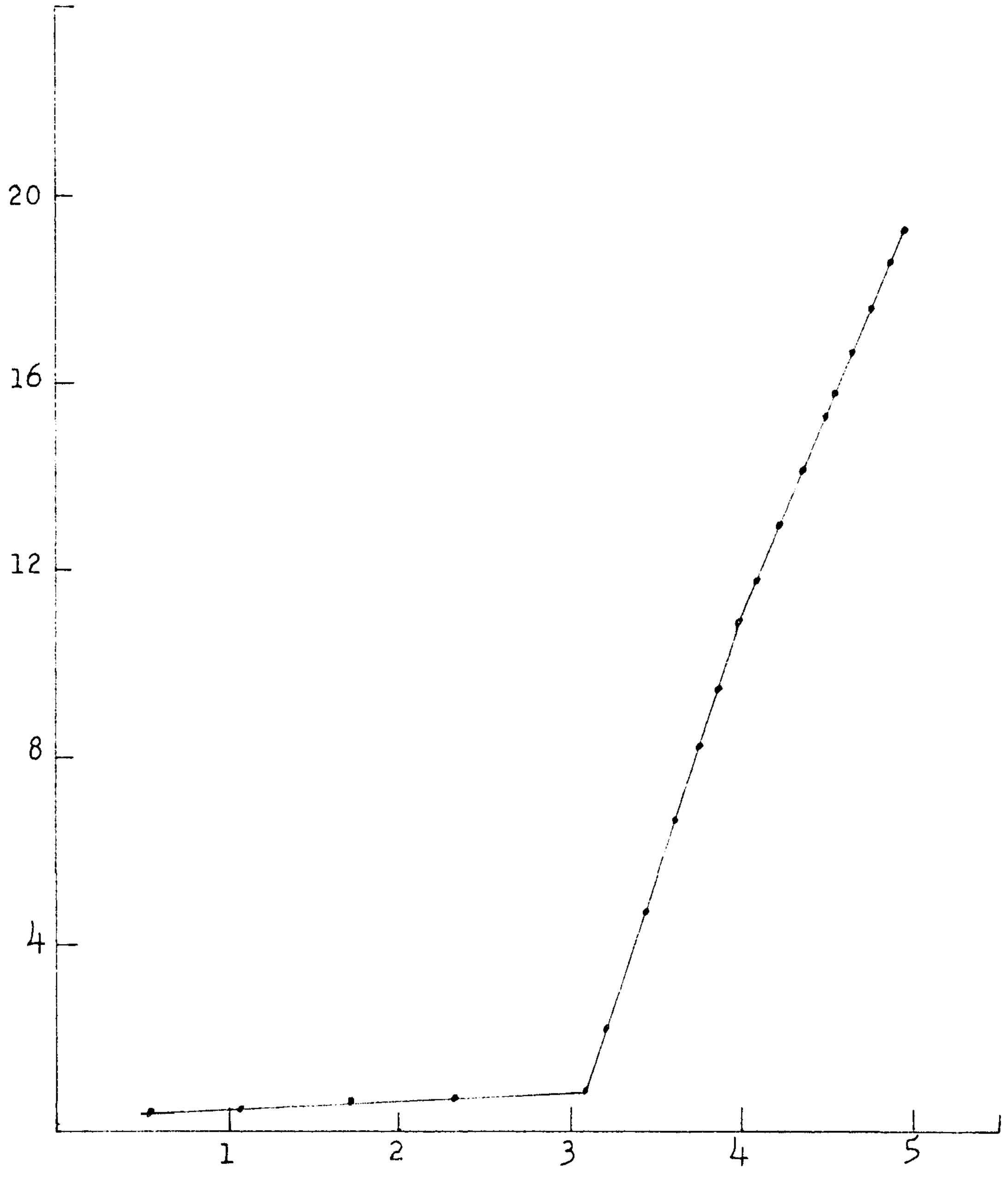

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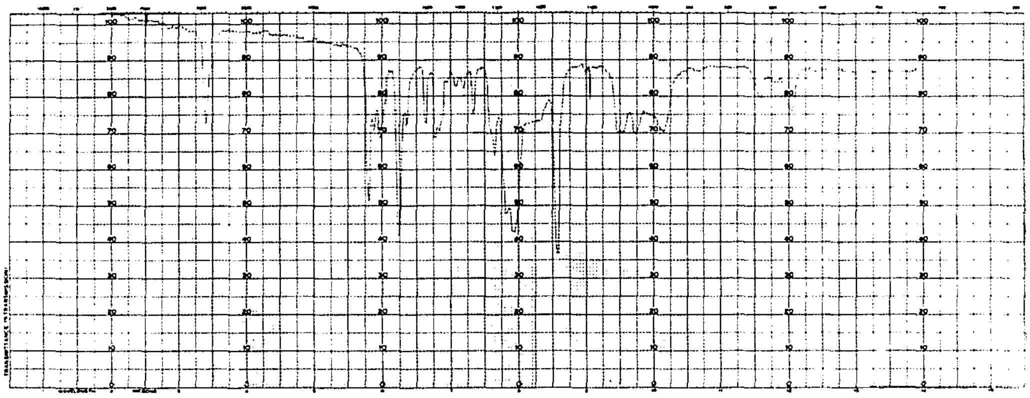
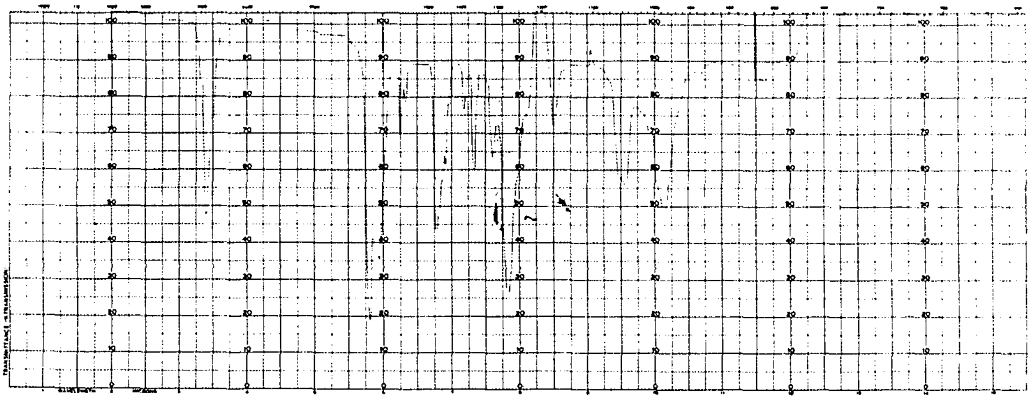
Figure 5. Infrared spectra of product of reaction of $Ni(DPM)_2$ with ρ-chlorobenzoyl chloride (top) benzoylchloride (bottom)

43b





used. The rate of the reaction became increasingly slow as the concentration of the reagents reached the value which corresponded to the completion of the reaction as predicted by the 2-1 stoichiometry.

Kinetics of tritylation of nickel DPM

The rate of tritylation at 50° was found to be second order as described by Equation 1.

$$(1) \quad \text{rate} = k_2 \left[\text{Ni(DPM)}_2\right] \left[C_6H_5COCl\right]$$

A plot of log $\frac{b(a-x)}{a(b-2x)}$ versus time is shown in Figure 6. Equation 2 was used to calculate the rate constant from the slope of the best straight line through the points.

$$(2) \quad kt = \frac{2.303}{(2a-b)} \log \frac{b(a-x)}{a(b-2x)}$$

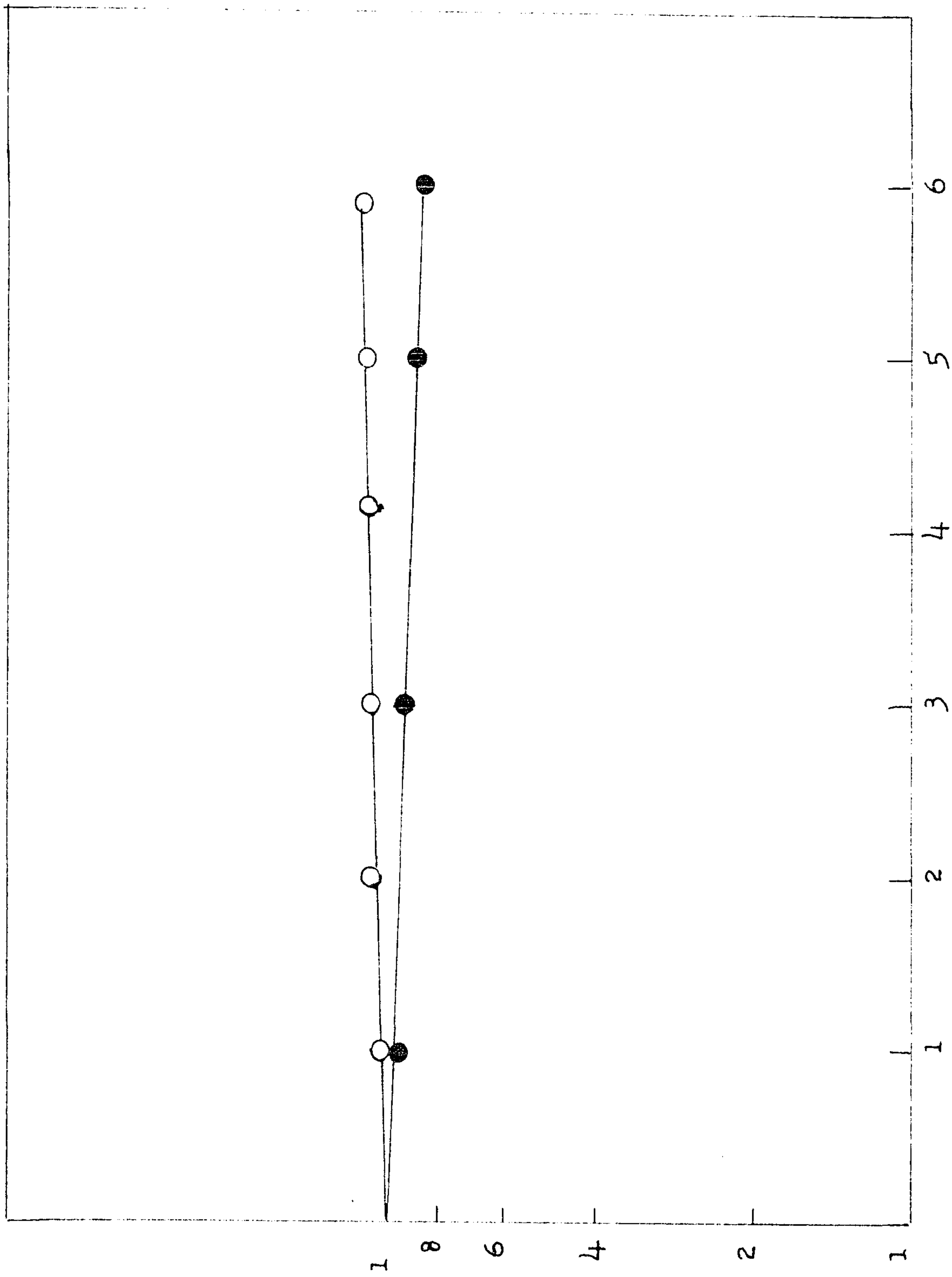
The rate is unchanged when anhydrous nickel chloride is present at the start of the reaction. More evidence that the reaction is not autocatalyzed by nickel chloride was realized when the second order plots of runs, which involved different initial concentrations, concided at points where respective concentrations became equal.

The tritylation is not catalyzed by the addition of DPM.

The rate could not be followed quantitatively when anhydrous aluminum chloride was added because the coloration produced by the added reagent interfered with the spectro-

Figure 6. Second order plot of tritylation of $Ni(DPM)_2$

abscissa - Time (hours)
ordinate - Log b/a (a-x)/(b-2x)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1
1
2
3
4
5
6

photometric determination of nickel DPM. Qualitative comparison of runs with and without aluminum chloride indicate that the reaction is about 100 times faster when aluminum chloride is added.

The studies of the kinetics of tritylation were carried out in a flask fitted with a condenser and drying tube. When the reaction was attempted in a stoppered flask, the rate slowed down. When the reaction vessel was flushed with nitrogen immediately after the reagents were added, no reaction was observed. This effect will be discussed further when the oxygen effects on the acylations of nickel DPM are described.

Kinetics of the benzoylation of nickel DPM

The rates of reaction of nickel DPM with benzoyl chloride were investigated at 50° and 60°. The reaction followed a second order rate law as described by Equation 1. Equation 2 was used to calculate rate constants at each point. The rate constants corresponding to first order dependence on benzoyl chloride were calculated using Equation 3.

$$(3) \quad k = \frac{2.303}{2t} \log \frac{b}{b-2x}$$

$b =$ original concentration of benzoyl chloride (moles/liter)

$x =$ amount of nickel DPM reacted (moles/liter)

The results of these calculations are shown in tables 4-8.

The second order rate constant for the benzoylation of nickel DPM at 50° is .019±.002 (liter-mole^{-1}-min^{-1}). When the reaction vessels were flushed with nitrogen and oxygen respectively, the oxygen rich reaction showed a much higher initial rate.

At 60°, the second order rate constant (Table 6) is .057±.002 (liter-mole^{-1}-min^{-1}). The rate is very sensitive to the purity of the benzoyl chloride used. After the standard solution was stored in a stoppered volumetric flask for a week, the rate of reaction of this sample was about twice that for the freshly distilled benzoyl chloride. If reagent grade benzoyl chloride is used without further purification, the rate is about 10-15 times faster than that observed with the freshly distilled reagent (Table 6).

The benzoylation is obviously catalyzed by impurities originally present in the benzoyl chloride and also by materials which are formed in the pure reagent. The most logical choice seems to be benzoic acid.

The rate of benzoylation is increased tenfold when aluminum chloride is added to the reaction. No catalytic effects were observed with nickel chloride or dipivaloylmethide.

Nickel pivalate dihydrate increases the reaction rate very slightly (Table 7). Anhydrous nickel pivalate is

Table 4. Rate of benzoylation of nickel DPM at 50°

Time (min.)	a-x	k_2 (liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-4}$ (min^{-1})
Flushed with oxygen		a = .0066, b = .0372	
45	.0064	.0855	1.22
120	.0060	.0197	1.23
240	.0057	.0169	1.04
480	.0050	.0163	0.94
540	.0048	.0167	0.94
660	.0045	.0166	0.90
950	.0038	.0185	0.92
1530	.0022	.0251	0.88
Flushed with nitrogen		a = .0068, b = .0372	
45	.0064	.0366	1.36
120	.0059	.0308	1.12
240	.0056	.0206	0.74
480	.0047	.0216	0.75
540	.0046	.0210	0.73
660	.0042	.0209	0.72
900	.0034	.0228	0.76
1530	.0019	.0266	0.82

a = original concentration of nickel DPM (moles/liter)

b = original concentration of benzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

probably much more soluble than the dihydrate in cyclohexane. The former would probably catalyze the reaction to a greater extent.

Table 5. Rates of benzoylation of nickel DPM at 60°

Time (min.)	b-2x	k_2(liter-mole^{-1}-min^{-1})	k_1 x 10^{-4}(min^{-1})
15	.0138	2.44	9.80
30	.0134	1.74	6.90
45	.0126	1.16	7.58
60	.0122	0.66	4.10
90	.0121	2.92	4.80
120	.0116	1.19	4.33
150	.0114	1.02	3.80
210	.0108	0.09	3.26
270	.0100	0.09	3.15
300	.0096	0.09	3.13
365	.0089	0.09	3.02
420	.0082	0.09	3.04
510	.0074	0.09	2.95
570	.0068	0.09	2.97
645	.0064	0.09	2.82
1185	.0048	0.08	2.06

a = .0093 - original concentration of nickel DPM (moles/liter)

b = .0148 - original concentration of benzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

Table 6. Rate of benzoylation of nickel DPM at 60°

Time (min.)	a-x	k_2(liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-4}$(min^{-1})
30	.0120	.0318	3.95
60	.0098	.1181	1.32
120	.0094	.0742	7.87
300	.0076	.0552	5.38
504	.0062	.0500	4.55
660	.0048	.0568	4.37
720	.0046	.0549	4.35
1110	.0029	.0596	3.55
1260	.0026	.0583	3.28

a = .0124 original concentration of nickel DPM (moles/liter)

b = .0348 original concentration of benzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

Kinetics of the reactions of nickel DPM with substituted benzoyl chlorides

Second order kinetics were found to describe the rates of *p*-methoxybenzoylation and *p*-chlorobenzoylation of nickel DPM. Typical calculated rate constants are shown in Tables 9-11. Difficulties in determining the rate law of these reactions were overcome only after the reactions were carried out in thoroughly degassed systems. Figure 7 shows a second

Table 7. Rate of benzoylation of nickel DPM at 60°

Time (min.)	a-x	k_2(liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-4}$(min^{-1})
30	.0102	.0798	8.29
90	.0080	.1147	10.5
120	.0073	.1124	9.97
300	.0054	.0840	6.45
390	.0050	.0744	5.39
540	.0042	.0677	4.58
690	.0036	.0625	3.98
780	.0035	.0575	3.59
1140	.0031	.0454	2.65
1320	.0027	.0449	2.44

a = .0110 original concentration of nickel DPM (moles/liter)

b = .0348 original concentration of benzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

order plot and a first order plot (first order with respect to p-CH_3-O-C_6H_5COCl). These plots indicate a better fit to a first order rate law. A second order rate law was definitely demonstrated in runs in which the system was degassed (Table 10).

The purities of these acylating agents were determined by potentometric titrations of acyl halide-methanol mixtures with aqueous sodium hydroxide. Figure 8 shows the results of

Table 8. Rate of benzoylation of nickel DPM at 60°

Time (min.)	a-x	k_2 (liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-4}$ (min^{-1})
10	.0074	.440	3.43
25	.0070	.270	2.03
35	.0067	.265	1.95
60	.0062	.221	1.57
90	.0054	.233	1.54
120	.0045	.268	1.62
160	.0034	.324	1.70
195	.0032	.296	1.49
225	.0026	.327	1.49

a = .0082 original concentration of nickel DPM (moles/liter)

b = .0227 original concentration of benzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

typical titrations. The fact that no break was found in the vertical portion of the titration curves seemed to indicate the absence of detectable amounts of carboxylic acid. Therefore, anisoyl chloride and *p*-chlorobenzoyl chloride were used in most of the runs without further purification. A few reactions were followed using redistilled anisoyl chloride. The second order rate constants for those reactions were six times slower than those in which the commercial

Table 9. Rate of p-methoxybenzoylation of nickel DPM at 60°

Time (min.)	b-2x	k_2(liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-4}$(min^{-1})
92	.0073	.0307	1.26
180	.0063	.0609	2.40
210	.0065	.0439	1.70
240	.0064	.0421	1.67
300	.0062	.0396	1.57
420	.0058	.0375	1.47
540	.0051	.0433	1.63
570	.0048	.0476	1.80
600	.0050	.0410	1.56
630	.0050	.0391	1.49
1350	.0031	.0207	1.46
1440	.0028	.0219	1.53
1560	.0022	.0258	1.74
1740	.0019	.0263	1.75

a = .0095 original concentration of nickel DPM (moles/liter)

b = .0077 original concentration of p-methoxybenzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

reagent was used without further purification (Table 9).

The rate of benzoylation and p-methoxybenzoylation have been found to be very similar in most cases. Since the rates

Table 10. Rate of p-methoxybenzoylation of nickel DPM at 60°

Time (min.)	a-x	k_2 (liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-3}$ (min^{-1})
5	.0074	.640	4.88
13	.0079	.404	3.06
20	.0073	.189	1.43
30	.0062	.356	2.52
40	.0063	.257	1.82
50	.0065	.177	1.28
60	.0063	.171	1.21
80	.0052	.240	1.55
90	.0052	.336	1.45
175	.0033	.263	1.35
190	.0032	.258	1.29
205	.0030	.255	1.26
235	.0028	.242	1.14
280	.0022	.259	1.10

a = .0080 original concentration of nickel DPM (moles/liter)

b = .0250 original concentration of p-methoxybenzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

of benzoylation and p-methoxybenzoylation of nickel DPM are known to be enhanced by an impurity in the acylating agents, and, furthermore, since the catalysis of benzoylation by

Table 11. Rate of *p*-chlorobenzoylation of nickel DPM at 60°

Time (min.)	a-x	k_2 (liter-mole^{-1}-min^{-1})	$k_1 \times 10^{-3}$ (min^{-1})
5	.0074	.287	2.18
15	.0052	.661	4.22
20	.0047	.609	3.73
25	.0046	.508	3.09
30	.0033	.714	3.71
35	.0032	.635	3.25
40	.0031	.578	2.91
50	.0021	.681	2.89

a = .0079 original concentration of nickel DPM (moles/liter)

b = .0462 original concentration of *p*-chlorobenzoyl chloride (moles/liter)

x = amount of nickel DPM reacted (moles/liter)

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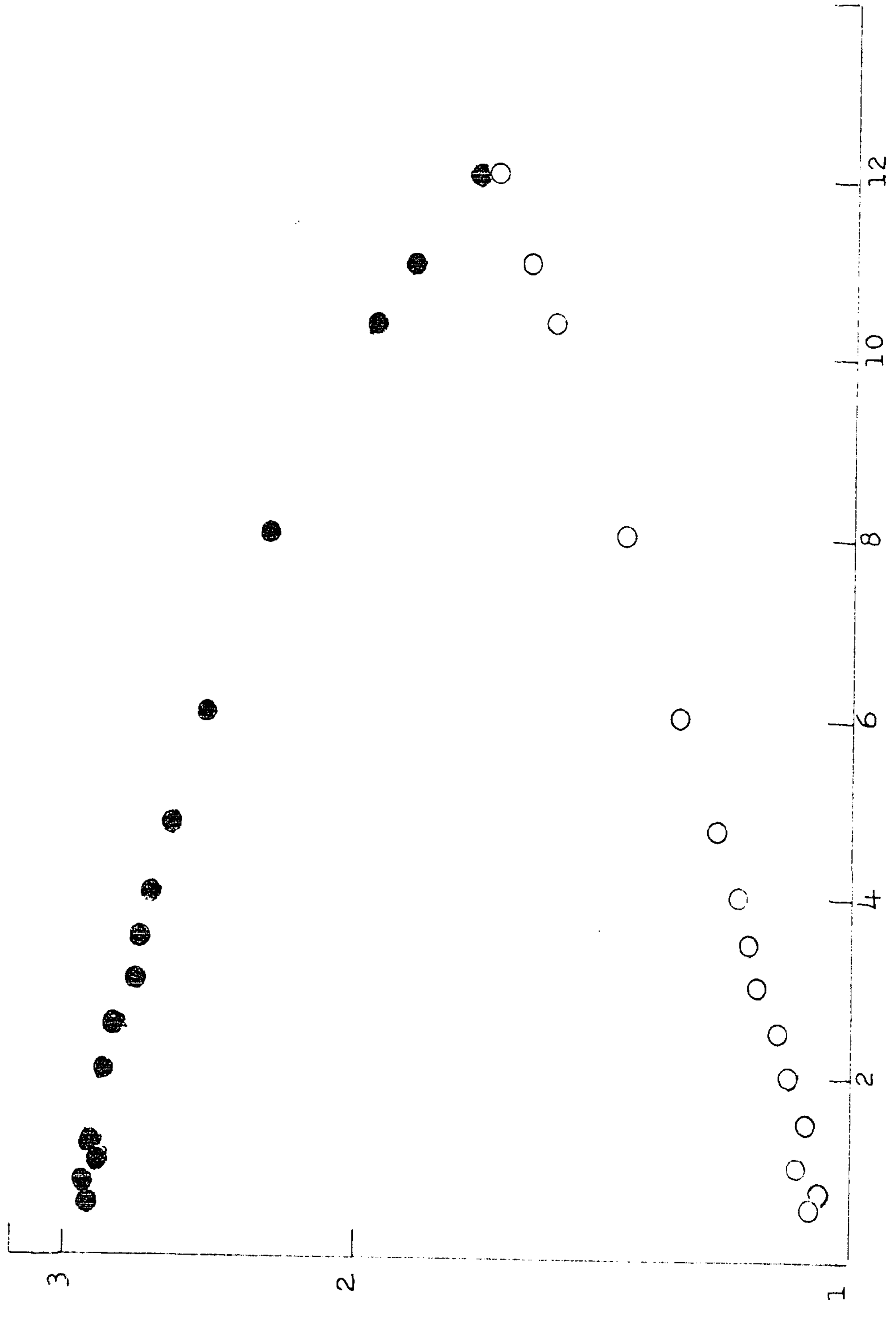
nickel pivalate has been demonstrated, the rates obtained in the *p*-chlorobenzoylation are very probably catalyzed rates. When the *p*-chlorobenzoylation was carried out in nondegassed systems, nickel pivalate was isolated from the reaction mixture. No nickel pivalate could be isolated from the benzoylation and *p*-methoxybenzoylation mixtures although the appearance of a green color on completion of the latter reaction indicated the possible presence of the oxidation product.

Figure 7. First order (○) and second order (●) plots of *p*-methoxybenzoylation of nickel DPM.

First order log $\frac{b}{b-2x}$ Second order log $\frac{b}{b-2x}$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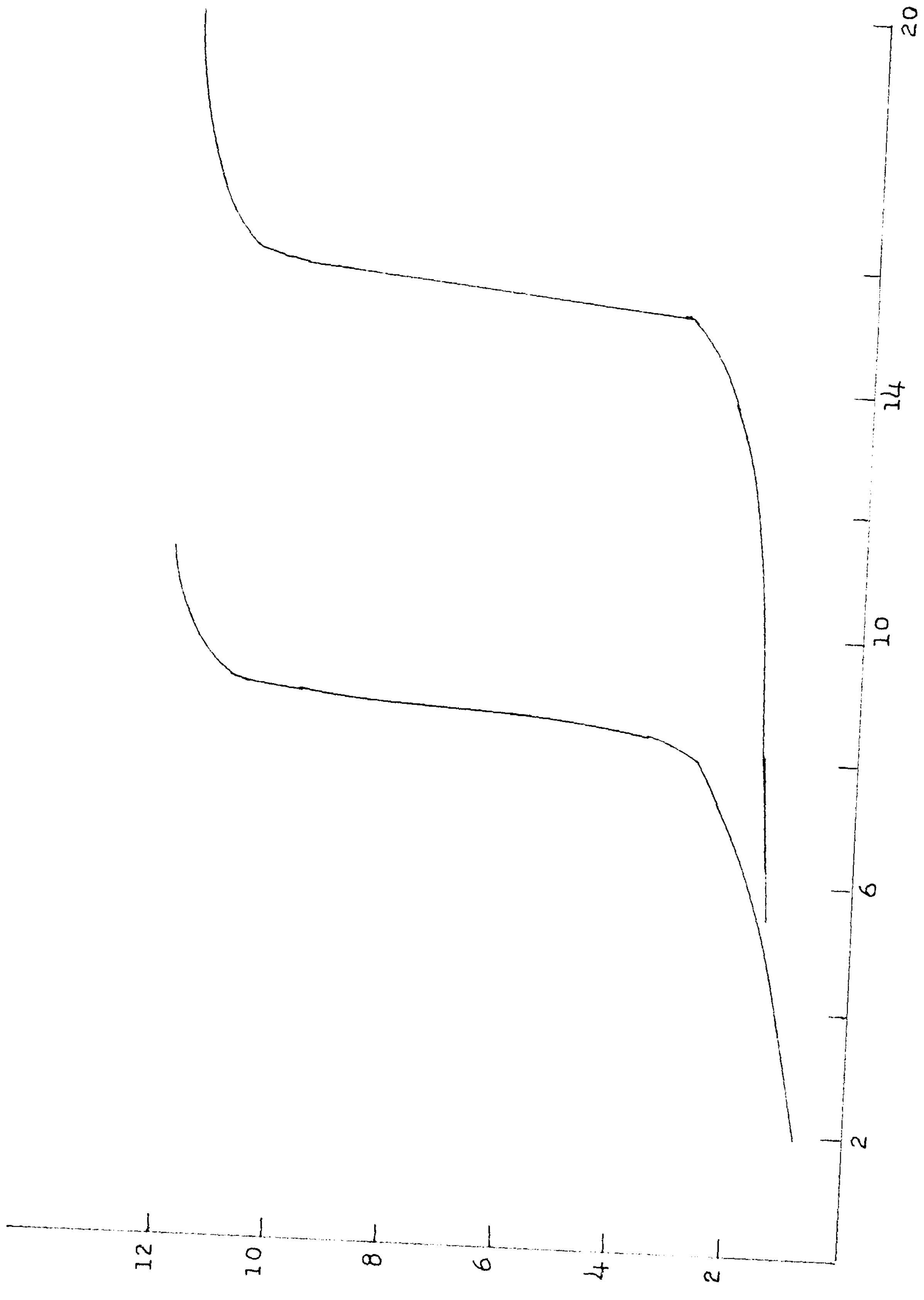
10
12

Figure 8. Potentometric titrations of acyl halide-methanol mixtures with aqueous sodium hydroxide

abscissa - Ml. base
ordinate - pH


2
4
6
8
10
12
2
6
10
14
20

The higher rate of *p*-chlorobenzoylation in degassed systems probably means that the latter contained a higher concentration of the catalyzing impurity which is probably the *p*-chlorobenzoic acid.

Mechanistic implication

A mechanism which accounts for the foregoing data might be formulated as follows:

$$(4)\quad \mathrm{Ni(DPM)_2 + 2RCOOH \longrightarrow 2H\text{-}DPM + Ni(RCOO)_2}$$

$$(5)\quad \mathrm{Ni(R\overset{O}{\overset{\|}{C}}\text{-}O)_2 + RCOCl \rightleftharpoons R\overset{+}{C}O\ \overset{-}{Cl}Ni(R\overset{O}{\overset{\|}{C}}\text{-}O)_2}$$

$$(6)\quad \mathrm{R\overset{+}{C}O\ \overset{-}{Cl}Ni(RCO_2)_2 + Ni(DPM)_2 \xrightarrow{slow} R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(DPM)_2}$$

$$(7)\quad \mathrm{R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(DPM)_2 + RCOCl \xrightarrow{fast} Products}$$

$$(8)\quad \mathrm{R\overset{O}{\overset{\|}{C}}\ Cl + Ni(DPM)_2 \xrightarrow{slow} R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(DPM)_2}$$

$$(9)\quad \mathrm{R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(DPM)_2 \xrightarrow{fast} Products}$$

$$(10)\quad \begin{matrix} \mathrm{R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(RCOO)_2} \\ \mathrm{or} \\ \mathrm{R\overset{+}{C}O\ \overset{-}{Cl}\ Ni(DPM)_2} \end{matrix} \quad + \quad \mathrm{O_2 \longrightarrow Oxidation\ products}$$

Equation 4 describes the fast reaction of nickel DPM and carboxylic acids. This would account for an initial fast rate which then settles down to a slower rate. Equations 5, 6, and 7 describe the catalyzed acylation process. If there really is an uncatalyzed reaction, it would be visualized as the process in equations 8 and 9. Since small amounts of acyl halides catalyze the oxidation of nickel DPM, this oxidation might proceed as outlined in equation 10.

A more thorough investigation of the catalytic effects postulated herein (especially the effects of the carboxylic acids and oxygen) is obviously needed in order to rigorously prove the mechanisms of alkylations and acylations of metal chelates of β-diketones.

SUMMARY

A study was made of the reactions of nickel dipivaloylmethide with the following reagents: tirphenylmethyl chloride, benzoyl chloride, *p*-chloro and *p*-methyl benzoyl chloride.

Infrared spectra of the easily hydrolyzed product of tritylation seem to indicate that the enol ether, the product of O-alkylation, is formed. The acyl halides react to give the triketones. The latter have been characterized by spectra and C, H, analysis.

The kinetics of all the reactions studied were found to settle down to a second order rate law after a fast initial reaction. The rate law is illustrated by equation 11:

$$(11) \quad \text{rate} = k_2 \left[\text{Ni(DPM)}_2\right] \left[\text{R-Cl}\right]$$

The trilylation did not take place at 50° when the reaction flask was flushed with nitrogen.

These reactions are catalyzed by aluminum chloride and nickel pivalate. The acylations are catalyzed by an impurity in the acyl chloride. When benzoyl chloride with different purity were used, the second order rate constant for the benzoylation of nickel DPM ranged from 0.02-0.20. The rate of *p*-methoxybenzoylation is the same as that for benzoylation. The *p*-chlorobenzoylations studied were about

twice as fast. The fast rate of the latter was attributed to the presence of a higher percentage of catalyst, which is probably the acid.

The air oxidation of nickel dipivaloymethide was found to compete with the acylations under the conditions of these studies. An investigation of this phenomenon showed that nickel pivalate is the major product. Pivalic acid was also detected in the product mixture. This oxidation takes place in chlorobenzene and in aromatic hydrocarbons. It occurs in cyclohexane when small amounts of benzoyl chlorides are present.

These results might be explained by the following sequence of reactions:

(1) $$\text{Ni(DPM)}_2 + \text{2RCOOH} \longrightarrow \text{2H-DPM} + \text{Ni9RCOO)}_2$$

(2) $$\text{Ni(R}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O)}_2 + \text{RCOCl} \rightleftharpoons \text{R}\overset{+}{\text{C}}\text{O}\ \overset{-}{\text{Cl}}\text{Ni(R}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O)}_2$$

(3) $$\text{R}\overset{+}{\text{C}}\text{O}\ \overset{-}{\text{Cl}}\text{Ni(RCO}_2\text{)}_2 + \text{Ni(BPM)}_2 \xrightarrow{\text{slow}} \text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}^{-}\text{Ni(DPM)}_2$$

(4) $$\text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}^{-}\text{Ni(DPM)}_2 + \text{RCOCl} \xrightarrow{\text{fast}} \text{Products}$$

(5) $$\text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}\ \text{Cl} + \text{Ni(DPM)}_2 \xrightarrow{\text{slow}} \text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}^{-}\text{Ni(DPM)}_2$$

(6) $$\text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}^{-}\text{Ni(DPM)}_2 \xrightarrow{\text{fast}} \text{Products}$$

(7) $$\left.\begin{matrix}\text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}\ \overset{-}{\text{Ni}}\text{(RCOO)}_2 \\ \text{or} \\ \text{R}\overset{+}{\text{C}}\text{O}\ \text{Cl}\ \overset{-}{\text{Ni}}\text{(DPM)}_2\end{matrix}\right. + \text{O}_2 \longrightarrow \text{Oxidation products}$$

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