ACTIVATION AND FUNCTIONALIZATION OF ALKANES

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Edited by

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Preface

Methods of activating or functionalizing alkanes have been numerous and well publicized in the past few years; as the most abundant class of organic compounds, alkanes constitute one of the greatest potential resources for chemical energy and for precursor compounds in organic synthesis. Both the abundance of alkanes and their extremely low reactivity have greatly interested a wide spectrum of chemical scientists. In the past five years investigators from several distinct subdisciplines of chemistry have made substantive contributions to the study of alkane activation or functionalization. The investigators who have concentrated on the development of liquid phase systems include a number of prominent organometallic chemists, bioorganic-bioinorganic chemists, and others. Paralleling this development in liquid phase methods have been equally strong experimental efforts by physical chemists and chemical physicists, the latter investigators examining both gas phase and solid state processes. In the early 1980s, when most of these programs were first developing, there appeared to be little communication among investigators in the different subdisciplines. For example, the chemical physicists had little awareness of the results and facts generated from studies directed toward liquid phase activation of alkanes by coordinatively unsaturated organometallic species. Similarly, the organometallic chemists had little awareness of the research on alkane activation in the gas phase, in spite of the fact that such awareness would have had widespread benefits for the conceptualization and understanding of the organometallic systems. Although cross-disciplinary communication and fertilization have improved substantially in the past five years, much more is possible and desirable. A factor present in 1989 that exacerbates the interdisciplinary communication problem is common to areas of research that spawn fundamentally new ideas, concepts, or methods: proliferation of the pertinent literature. In 1980 there were only a few papers that addressed new systems or investigations of alkane carbon-hydrogen bond cleavage of any kind. There are now on the order of 10^3 such publications.

This volume does not attempt to cover all areas of chemical research that address the activation or cleavage of alkane carbon-hydrogen bonds. To do this in a sensible and pragmatic manner within a single volume at this stage would be difficult, if not impossible. This book concentrates on the systems that are conceptually and practically closest to the first highly selective catalytic high-conversion alkane

functionalization processes to be developed in the future --
homogeneous processes, and largely those in the liquid phase. The
goals of this book are twofold:

1. To provide in one volume discussions of most of the principal
approaches to transforming alkanes so that the energetic and mechanistic
features as well as the preparative potential of these processes can be
examined in relation to one another.

2. To bring together in one volume most of the principal methods
for activating or functionalizing alkanes that are currently of interest to
preparative chemists or should ultimately lead to processes that are of
interest to these investigators.

The book begins with a chapter by A. E. Shilov of the U.S.S.R.
Academy of Sciences, one of the early pioneers of alkane activation in
the liquid phase. His chapter addresses both the early work and more
recent biomimetic approaches from his laboratory and those of his
colleagues. The second chapter by G. A. Olah et al. outlines the
activation of alkanes by superacid and other electrophilic systems, work
that predates most of the alkane chemistry effected by organometallic,
metalloporphyrin, and other systems, but which remains unique and yet
in many ways complementary to all other homogeneous alkane
activation or functionalization processes in the literature. In Chapters
III, IV, and V, some of the most prominent investigators in their
respective areas describe three increasingly distinct types of
organometallic systems that activate alkanes. Nearly all the work in
these chapters involves research done since the first reports of
nonradical C-H bond activation facilitated by transition metal complexes
reported by R. H. Crabtree and R. G. Bergman in early 1982. R. H.
Crabtree in Chapter III discusses alkane activation by the polyhydride
complexes, including those few organometallic compounds that
catalytically transform alkanes, as well as a new highly catalytic and
selective approach involving photosensitized Hg vapor. In Chapter IV,
W. D. Jones discusses the alkane chemistry seen in the cyclopentadienyl
rhodium, iridium, rhenium, and related systems. The stoichiometric
alkane activation reactions effected by these complexes have produced a
wealth of important energetic and mechanistic information. In Chapter
V, I. P. Rothwell reviews C-H bond activation in the d^0 transition
metal systems. Some of these systems investigated primarily by the
groups of I. P. Rothwell, P. L. Watson, and T. J. Marks have
generated substantial new chemistry, including the first reported
organotransition metal species capable of activating methane. Chapters
VI and VII and a portion of Chapter X address the homogeneous
catalytic functionalization of alkanes by metalloporphyrins. Most of the
molecular features of hydrocarbon transformation by these compounds
are distinct from those seen in the organometallic systems. In Chapter
VI, D. Mansuy and P. Battioni describe some of the alkane

functionalization experiments involving the enzyme cytochrome P-450, the principal catalyst for hydrocarbon oxidation in the biosphere, as well as cytochrome P-450 metalloporphyrin model compounds, using two of the most biologically and industrially available oxidants, hydrogen peroxide and dioxygen. In Chapter VII, K. S. Suslick focuses on the modification of metalloporphyrin catalysts to facilitate the shape-selective hydroxylation of alkanes. Chapters VIII and IX describe hydrocarbon oxidation systems unlike any others in the literature. In Chapter VIII, C. L. Hill reviews the literature on oxo transfer to alkanes and describes alkane oxygenation by transition metal-substituted polyoxometalates, complexes that effectively represent homogeneous inorganic metalloporphyrin analogs that are thermodynamically, not just kinetically, resistant to oxidation. The new catalytic selective photochemical methods for the functionalization of alkanes based on polyoxometalates developed by the Hill group are not reviewed here but will be reviewed elsewhere in the near future. In Chapter IX, D. H. R. Barton and N. Ozbalik address several aspects of the "Gif" system for C-H functionalization. Some of the mechanistic attributes of this unique chemistry as well as its application to synthetic problems are presented. In the final chapter, C. A. Tolman, J. D. Druliner, M. J. Nappa, and N. Herron, all contributors to problems associated with alkane oxidation or functionalization themselves, collectively address the substantial alkane oxidation research, practical and exploratory alike, that has garnered serious attention for more than two decades in Du Pont's Central Research & Development Department.

Although the methodologies and the basic scientific information pertaining to the activation and functionalization of alkanes as well as unactivated C-H bonds in more complex molecules is still advancing rapidly and minor aspects of this book will be dated by publication time, the in-depth discussions of mechanism, structure-reactivity information, and other aspects of this chemistry should ensure the lasting value of this monograph. Given the continuing advances in the subject areas of this book and the consequent limited shelf life of a portion of the research, we chose to produce the entire book in a camera-ready but print quality format using a laserwriter printer system in my office rather than using the normal typesetting procedure. The former procedure although faster, in principle, than the latter, proved to be a very substantial amount of work -- translation: a full time job for a highly competent secretary for one year. It is with this fact articulated that I give my tremendous gratitude to my two secretaries that worked on this project, Deborah Finn and Nithya Raghunathan. Without them the entire project would have been impossible. Deborah Finn started this opus and contributed a great deal to the editing, organizing, and other tasks in the early stages. Nithya Raghunathan took over most of the aspects of production for a period of 7 months making mistakes so rarely that it became a point of some amusement when she made one. It is unusual to have one secretary as professional, dedicated, and competent as either Deborah or Nithya; it is rare indeed to have been

blessed with two of them. Again, they have my admiration and deep felt thanks.

CRAIG L. HILL

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Contents

Chapter I

HISTORICAL EVOLUTION OF HOMOGENEOUS ALKANE ACTIVATION SYSTEMS

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I.   Introduction

Since the end of the 1960s a new problem has arisen in the field of homogeneous catalysis, that of homogeneous activation of saturated hydrocarbons by metal complexes. The development of coordination chemistry and catalysis had lead to increased success in the activation of various molecules by metal complexes, such as hydrogen, olefins, aromatics, carbon monoxide, and molecular nitrogen. "Activation" of a certain molecule by a metal complex, although a rather vague concept, usually means that the molecule or its part becomes a ligand in the coordination sphere of the complex and then undergoes a subsequent chemical transformation.

For some time saturated hydrocarbons remained outside of this process, which involved all the other classes of organic and inorganic substances. Meanwhile, an increasingly urgent problem involved the great resources of natural gas that necessitated the creation of new selective processes involving methane, which constitutes its primary part. At the same time, the activation of methane and its analogs is an interesting theoretical problem, since the absence of double or triple bonds, lone electron pairs, and the strength of covalent C-H and C-C σ-bonds in alkanes constitute natural difficulties in the search for desirable systems.

In 1968 J. Halpern[1], one of the leading specialists in homogeneous catalysis, described the task as "to develop a successful

approach for activation of C-H bonds, particularly saturated hydrocarbons, this problem being at present one of the most important and challenging in the entire field of homogeneous catalysis."

The chemical inertness of alkanes is well known and is reflected in one of their old names, "paraffins" (from the Latin *parum affinis* - without affinity). The alkane reactions known in chemistry usually require particularly active particles, e.g., strong oxidants, superacids, free atoms, radicals, and carbenes, or proceed at high temperatures or require other sources of energy (as in radiation chemistry.)

In the 1960s it was possible to suggest the existence of other more selective reactions of alkanes under comparatively mild conditions. The bases for such suggestions are summarized as follows:

1. The σ-bond in molecular hydrogen is not weaker than the σ-C-H bond in alkanes. However, multiple examples of homogeneous H_2 activation are known, for example -in H-D exchange or hydrogenation. Therefore an analogy with H_2 activation could be used in the search for alkane catalytic reactions in solution.[*]

2. A number of metal complexes (ML_n or M) are capable of reacting with substances containing "activated" C-H bonds, e.g., C-H bonds in aromatic hydrocarbons or in the α-position to double bonds. The C-H bond is being cleaved in this reaction and an M-C bond is formed. Therefore the C-H bond energy, which in aromatic compounds is even higher than in alkanes, does not prevent the reaction.

3. A "nonactivated" aliphatic C-H bond may be involved in the reaction when it is present in a suitable position in a ligand of the complex coordination sphere. The result of the reaction is often cyclometallation. This reaction indicates the possibility of a similar reaction (perhaps at high temperatures) of alkanes.

4. Since the 1930s facile alkane reactions at the surface of metals and oxides have been known, in which the C-H bond is definitely cleaved, e.g., in H-D exchange with D_2. Similar reaction may be visualized in homogeneous solutions, at least for polynuclear complexes.

5. Enzymatic oxidation is known including hydroxylation of C-H bonds in saturated hydrocarbons catalyzed by metal enzymes. For example, the methane monoxygenase catalyzes methane oxidation primarily to methanol. Mechanistic investigation of these processes may help to use a biomimetic approach to create similar purely chemical catalytic systems.

Beginning in the 1960s, investigations directed to the activation of alkanes and to the discovery of new catalytic reactions involving the

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[*]The analogy of alkanes with other compounds from the viewpoint of the search for their activation is considered more thoroughly by Shilov.[2] More references on different sources can also be found there.

participation of metal complexes were conducted along several main routes.

II.   Homogeneous Activation of Alkanes by Platinum(II) Complexes

In the search for a successful approach to C-H bond activation in alkanes (RH) and using the analogy with H_2 activation we could suggest an oxidative addition of an alkane to the coordinatively unsaturated complex of a transition metal:

$$L_nM \ + \ RH \ \rightleftharpoons \ L_nM\Big\langle{}^R_H$$
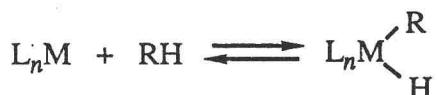
The reaction may be reversible and shifted to the left, taking into account the strong C-H bond and comparatively weak M-R and M-H bonds.

Therefore there must be some indication that the oxidative addition does take place, even though the equilibrium is shifted to the left. The simplest consequence of equilibrium 1 may be H-D exchange with D_2, solvent, or other substances present in the solution. In particular H-D exchange may be expected with the solvent protons if the alkyl hydride complex formed primarily has sufficiently strong acid properties.

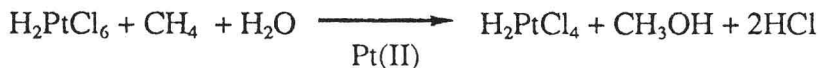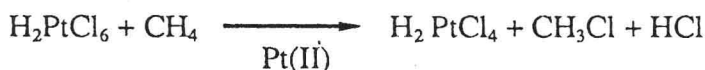$$L_nM\Big\langle{}^R_H \ \rightleftharpoons \ L_nM\text{-}R^- + H^+ \tag{1}$$
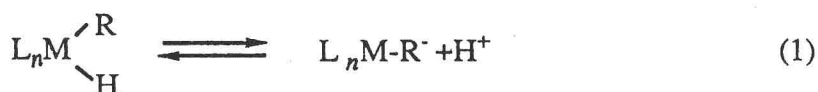
At the end of the 1960s no such examples were known. It was natural to start with the simplest systems. Therefore, our attention was attracted to the works by Garnett and Hodges, who had shown that ordinary platinum(II) complexes, $PtCl_4{}^{2-}$, catalyze the H-D exchange of aromatic hydrocarbons with the solvent in a water-acetic acid mixture.[3] Hydrogen atoms involved in the exchange with the protic solvent had been shown to include not only those of the aromatic ring but also of its side chain, including ß-H atoms, e.g., H atoms of the methyl group in ethylbenzene. Garnett and Hodges[3] postulated the formation of π-complexes of Pt(III) with the aromatic ring as a necessary precondition of C-H bond activation. However, another alternative should be taken into account, i.e., direct attack of the Pt(II) complex at the nonactivated C-H bond. To our surprise this first and simplest system did indeed work: methane and ethane revealed their ability to
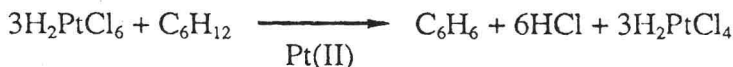
exchange catalytically their H atoms for deuterium of the solvent at 90-120°C in the presence of a chloride complex of bivalent platinum.[4] Moreover, it became clear afterward that the species present in the water-acetic acid solution of the well known Pt(II) complex (K_2PtCl_4) contains the most active catalysts of the H-D exchange. The use of other metals with Cl^- or other ligands with Pt(II) leads to either a decrease in the reaction rate or to a complete stoppage of the reaction.

Catalytic H-D exchange of alkanes with water in the presence of Pt(II) complexes could have been discovered much earlier, e.g., in 1930s, when H-D exchange of alkanes with D_2 was found at metal surfaces. Apparently the chemical inertness of alkanes inhibited the search for reactions catalyzed by simple Pt(II) complexes.

According to Reaction 1 the mechanism of H-D exchange has to involve alkyl platinum derivatives. In view of the reactivity of alkyl groups bound to metal, other reactions could be expected under the same conditions as those for H-D exchange. Such reactions soon were found.[5] Platinum(IV) complexes turned out to be capable of oxidizing alkanes in the presence of Pt(II) to chlorides and (as found later) alcohols. For example, methane reacts according to the equations:

$$H_2PtCl_6 + CH_4 \xrightarrow{\quad Pt(II) \quad} H_2 PtCl_4 + CH_3Cl + HCl$$

$$H_2PtCl_6 + CH_4 + H_2O \xrightarrow{\quad Pt(II) \quad} H_2PtCl_4 + CH_3OH + 2HCl$$

Dehydrogenation proceeds in the case of cyclohexane:

$$3H_2PtCl_6 + C_6H_{12} \xrightarrow{\quad Pt(II) \quad} C_6H_6 + 6HCl + 3H_2PtCl_4$$

These were the first examples of alkane homogeneous functionalization catalyzed by electron-rich complexes (see below).

In the presence of the external oxidant (dioxygen) and electron transfer agent ($CuCl_2$, quinones, heteropolyacids) the system H_2PtCl_6-H_2PtCl_4 can become catalytic with respect to both platinum compounds. However, the turnover number is small, primarily because of secondary reactions, e.g., oxidation of methanol in the case of methane.

Further investigations of alkane H-D exchange and oxidation in the presence of platinum complexes were conducted in several research groups by Garnett et al. in Australia, Webster and Hodges in Great Britain[6] and Rudakov[7] and Shilov[2] the U.S.S.R. In all cases the results obtained were similar and mutually complementary. They can be summarized as follows:

1. H-D exchange and oxidation by H_2PtCl_6 involve the same intermediate, which is presumably the alkylated complex of Pt(II): $RPtClL_2$ (L is the H_2O or HOAc). The result is that when the formation of this intermediate is a rate-determining step [temperature below 100°C, high Pt(IV) concentrations] the rate of H-D exchange in the absence of Pt(IV) coincides with that of oxidation under the action of H_2PtCl_6.

2. Among the Pt(II) complexes both positive, $PtClL_3^+$, and negative, $PtCl_3L^-$, ions are active toward alkanes as well as uncharged $PtCl_2L_2$ (Table I). Symmetrical PtL_4^{2+} and $PtCl_4^{2-}$ are inactive.

Table I. Rate Constants (mol^{-1} liter sec^{-1}) of Reactions of PtL_4^{2+} (k_0), $PtClL_3^+$ (k_1), $PtCl_2L_2$ (k_2), $PtCl_3L^-$ (k_3), and $PtCl_4^{2-}$ (k_4)
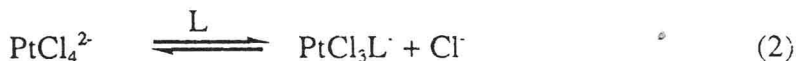
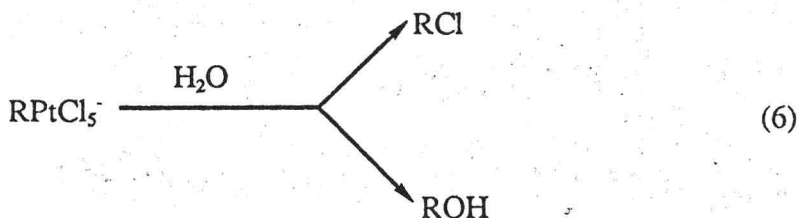| Hydrocarbon	k_0	k_1	k_2	k_3	k_4
Isobutane	0	1.9±0.1	3.8±1.1	3.7±0.1	0
Cyclohexane	0	5.3±0.2	9.5±2.4	12±0.3	0
Benzene	9.1±1.4	66±31	12±4	18±2	0

Source: From Rudakov et al.[7b]

Introduction of "softer" ligands in the platinum coordination sphere as phosphines or dimethyl sulfoxide (DMSO) slows down the reaction. The order of reactivity in reaction of alkanes is inverse to the trans-effect observed for substitution reactions in Pt(II) complexes.

3. With respect to the series of alkanes, platinum(II) complexes behave as moderate electrophiles (the rate increases in the order $CH_4 < C_2H_6 < C_3H_8$). Steric factors play an important role. Isolated methyl groups are the most active. Methyl and methylene groups situated next to bulky *tert*-butyl group display very little activity. Tertiary C-H bond is not active at all.

Kinetic investigation leads to the following reactions:

$$PtCl_4^{2-} \overset{L}{\rightleftharpoons} PtCl_3L^- + Cl^- \tag{2}$$

$$PtCl_3L^- \overset{K}{\rightleftharpoons} PtCl_2L_2 + Cl^- \tag{3}$$

$$PtCl_2L_2 + RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RPtClL_2 + H^+ + Cl^- \tag{4}$$

$$RPtClL_2 + PtCl_6^{2-} \overset{k_2}{\longrightarrow} RPtCl_5^{2-} + PtCl_2L_2 \tag{5}$$

$$RPtCl_5^- \xrightarrow{\quad H_2O \quad} \begin{array}{l} \nearrow RCl \\ \\ \searrow ROH \end{array} \qquad (6)$$

The following kinetic equation corresponds to this scheme, provided the stationary state is reached:

$$(k_1[PtCl_2L_2][RH] = k_{-1}[RPtClL_2][H^+][Cl^-] + k_2[RPtCl_2L_2][PtCl_6^{2-}])$$

$$-\frac{d[Pt(IV)]}{dt} = \frac{k_1 k_2 K[RH][Pt(II)][Pt(IV)]}{([Cl^-] + K)(k_{-1}[H^+][Cl^-] + k_2[Pt(IV)])}$$

In the absence of Pt(IV) Reaction 4 leads to the H-D exchange with the solvent. At the addition of Pt(IV) the H-D exchange rate decreases, the sum of the rates [exchange and oxidation by Pt(IV)] remaining constant.[7a] This is the evidence for the same intermediate (RPtClL_2) formed with the constant rate $k_1[PtCl_2L_2]$ [RH].

Kinetic curves for methane oxidation are shown in Figure 1.[8] The product is the complex of Pt(II), which is the catalyst of the process, and the reaction rate initially increases with time. Methyl chloride and methanol are seen to form in parallel reactions, approaching quantitative yield per oxidant.

To prove Reactions 2 - 6, it was essential to provide evidence for the formation of the alkyl platinum intermediate. Some indirect data supported this view. For aromatic compounds arylplatinum(IV) complexes are sufficiently stable to be isolated and in some cases structural analysis has been made. Platination of aromatic compounds by Pt(IV) turned out to be a very effective way to synthesize these complexes (see ref. 9 for a review).

For alkanes, e.g., methane, the reaction temperature is higher and expectations of observing the intermediate in water as a solvent were not particularly high. However, such an intermediate was detected, first by chemical analysis (Fig. 1) and then directly by NMR spectroscopy (Fig. 2). Moreover, kinetic analysis has shown that the entire process proceeds via the alkylated Pt(IV) complex $CH_3PtCl_5^{2-}$.
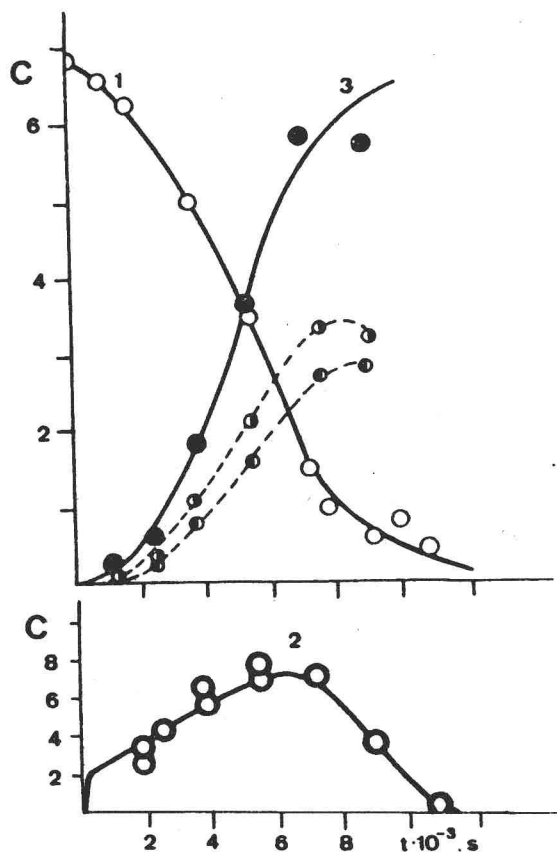
FIGURE 1. The kinetic data on Pt(IV) consumption (curve 1, O, [Pt(IV)] x 10^2, M); methylplatinum(IV) complex behavior (curve 2, ◐, [Pt(IV)-CH_3] x 10^5, M), the total of products accumulation (curve 3, ●, [CH_3OH] + [CH_3Cl]) x 10^2, M), and the accumulation of methanol (◐, [CH_3OH] x 10^2, M) and methyl chloride (◐, [CH_3Cl] x 10^2, M) in the reaction of methane with an aqueous solution of platinum chloride complex; 120°C, [CH_4] = 0.1 M, [K_2PtCl_4]_0 = 1.5 x 10^{-2} M.

Its decomposition rate was measured separately, the products being the same as for the CH_4 oxidation, i.e., Pt(II) and CH_3Cl together with CH_3OH. Extrapolating the temperature dependence of the rate constant to the temperature of the methane reaction with H_2PtCl_6 in the presence of Pt(II) and knowing the experimental value of CH_3PtCl_5^{2-} concentration in the reaction mixture, it was possible to calculate the reaction rate for decomposition of this complex under the reaction conditions. The calculated reaction rate was found to coincide quantitatively with the observed overall reaction rate of Pt(IV) consumption.