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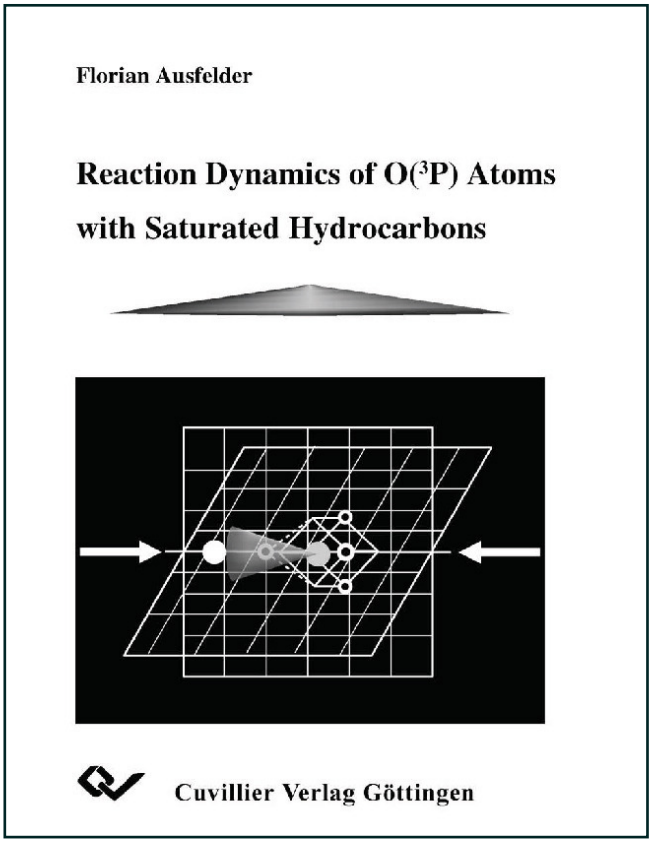
# Reaction Dynamics of O(3P) Atoms with Saturated Hydrocarbons

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# Chapter 1: Introduction

## 1.1 General introduction

The aim of reaction dynamics is to understand the path a chemical reaction takes to change the reactants into the products. It is at the very heart of chemistry, trying to establish the rules that govern a given chemical process.

Even though chemical reactions are constrained by the conservation of energy and angular momentum, they display an astonishing variety of different mechanisms. A chemical reaction is a delicate system of balance involving energy and angular momentum in its different forms. Trying to establish the accurate "balance sheet" for a given reaction, even as simple as $H + H_2$, is a very difficult task.

Experiments usually only manage to pin down a few details and the theoretical effort, even though huge progress has been made, is still struggling to keep up with the experimental work for all but the most basic reactions. In a few areas, experimental work and theoretical effort stimulate each other, pushing the border of understanding slowly forward.

The following study is set in one of these areas. In parallel with this experimental study, contemporary new calculations deepened the insight into the systems dramatically.

Far from having just a confirmative role, experiments provide the ultimate test for the calculations, and more importantly, also shed light on aspects not yet well understood theoretically.

## 1.2 Introduction to the reactions of oxygen atoms with saturated hydrocarbons

Reactions of oxygen atoms with hydrocarbons are of broad interest in many applied fields ranging from high temperature combustion processes, through atmospheric processes to degradation of plastics in near-earth orbiting spaceships. In addition they represent the simplest form of oxidation that can be imagined for an alkane.

The two lowest electronic states of the oxygen atom, $O(^3P)$, the electronic ground state, and $O(^1D)$, the first electronically excited state, which lies about 190 kJ $mol^{-1}$ higher in energy, show very distinct behaviours. While the general reaction of oxygen atoms with a saturated hydrocarbon, where R denotes an alkyl group,

$$O + HR \rightarrow R + OH \qquad \text{reaction (1.1)}$$

remains valid for both cases the products are formed in very different ways.

In the case of $O(^1D)$, a large fraction of the reactive flux is thought to involve insertion of the incoming $O(^1D)$ atom into an existing bond to form a relatively long-lived H-O-R alcohol intermediate following reaction (1.2).

$$O(^1D) + HR \rightarrow [HOR] \rightarrow R + OH \qquad \text{reaction (1.2)}$$

In addition, if the hydrocarbon is not $CH_4$, C-C bond rupture may occur in competition with the C-O bond fission in the alcohol intermediate.

On the other hand, it is generally thought that the analogue reaction with a ground state oxygen atom $O(^3P)$ proceeds via a collinear H atom abstraction as shown in reaction (1.3).

$$O(^3P) + HR \rightarrow [O\text{--}H\text{--}R] \rightarrow OH + R \qquad \text{reaction (1.3)}$$

The extent to which these limiting pictures are supported by experimental data and theoretical calculations will be discussed in detail in the following sections.

For a long time most dynamical studies focussed on reaction (1.2) mainly because its energetics are very favourable. Reactions of class (1.2) tend to be hugely exothermic and essentially barrierless. The reaction rate, which is close to the gas kinetic limit [1,2,3,4], shows hardly any temperature dependence [5]. This makes reaction (1.2) easily accessible for experimental studies even for the parent molecule $CH_4$ which has the least favourable energetics. The reaction passes over a deep potential well which corresponds to the stable methanol molecule. Photolytically generated $O(^1D)$ provides, for example, an important mechanism for the oxidation of hydrocarbons in the atmosphere [6].

This is not the case for $O(^3P)$, however, for which the high barriers more than offset its greater abundance. Experimental work is hampered by the much less favourable energetics. Reactions of the type (1.3) have in general a significant barrier which increases in the order tertiary < secondary < primary < $CH_4$ and an exothermicity which changes in the opposite direction making the reaction of $O(^3P)$ with $CH_4$ even slightly endothermic. A compilation of the thermodynamic data can be found in reference [7]. A schematic representation of the reaction profile is shown in figure 1.1.

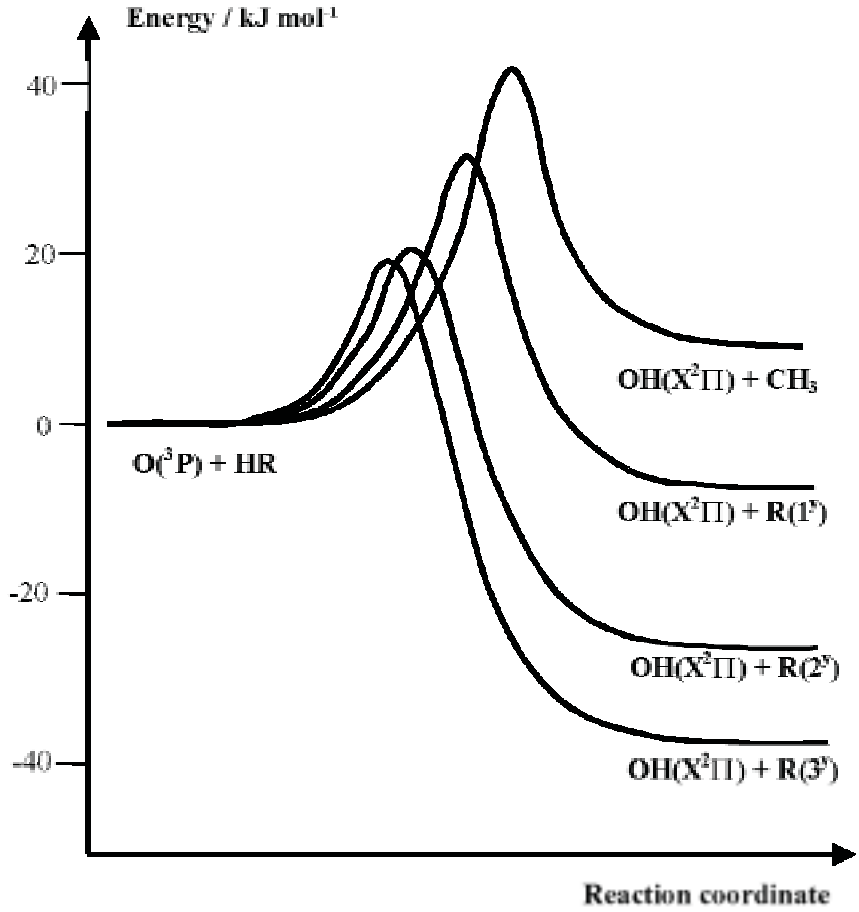


Figure 1.1: Schematic reaction profiles for $O(^3P)$ + saturated hydrocarbon reactions. Adapted from a similar diagram in [14].