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The dynamics of $O(^{3}P)$ + deuterated hydrocarbons: influences on product rotation and fine-structure state partitioning

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The dynamics of the reactions $O({}^{3}P) + CH_{4}/CD_{4}$ and $O({}^{3}P) + cyclo-C_{6}H_{12}/C_{6}D_{12}$ have been investigated experimentally. Translationally hot $O({}^{3}P)$ atoms were generated by laser photolysis of NO₂ at 266 nm. The rotational and fine-structure state distributions in the nascent product OH or OD radicals were determined by laser-induced fluorescence. The deuterium-labelled reactants have provided confirmation of the main features of the product-state partitioning observed previously for normal-hydrogen compounds. Only OH v' = 0is detectable from CH_4 . CD_4 also produces predominantly OD v' = 0, with v' = 1 being just detectable with an estimated branching ratio of ~ 0.06. Both cyclo- C_6H_{12} and C_6D_{12} produce significant yields of v' = 0 and 1 products. Despite the opposite trend in exothermicities, the v' = 0 products are rotationally hotter from methane than from cyclohexane, indicative of a stereochemical effect. The absolute rotational energy release is in each case found to be essentially independent of hydrogen isotope. It is argued that this supports the accepted collinear abstraction mechanism for this class of reactions. The OH fine-structure state partitioning is not influenced by hydrogen isotope, nor by product vibrational level despite distinct differences in the associated rotational energy release. This appears consistent with a previously derived model involving selected nonadiabatic coupling of adiabatic electronic fine-structure surfaces.

Introduction

The reactions of $O({}^{3}P)$ atoms with saturated hydrocarbons are of practical importance in high temperature combustion. There have consequently been many conventional kinetic measurements of their rate constants.¹⁻⁴ They are also of interest fundamentally, stimulating investigations of their dynamics. Comparatively speaking, however, they have received much less attention in this respect than their cousins, the reactions of $O({}^{1}D)$ with hydrocarbons. This is primarily for experimental reasons, because the relatively large barriers, first established kinetically, require high collision energies and make product yields low. Nevertheless, the $O({}^{3}P)$ reactions are an interesting class because they appear to be at the opposite end of the dynamical spectrum from the $O({}^{1}D)$ reactions, involving direct abstraction in contrast to transient insertion.

Previous work on the dynamics of the $O(^{3}P)$ + hydrocarbons, and some related reactions, is the subject of a recent review⁵ and so only a concise summary will be given here. From an experimental point of view, the first insight was gained through the ground-breaking work of Andresen and Luntz.⁶ They first introduced the use of laser-induced fluorescence (LIF) detection to determine product state distributions in the product OH. A series of representative primary, secondary and tertiary hydrocarbons was examined. Similar studies followed in the groups of Whitehead^{7,8} and McKendrick,⁹ with the introduction of laser photolysis for $O(^{3}P)$ generation in place of the discharge methods used originally. Significantly, this allowed the OH from parent reaction, $O(^{3}P) + CH_{4}$, to be studied for the first time.⁹ This reaction requires the highest laboratory frame translational energies because it has the highest activation barrier in conjunction with the least favourable kinematics. Undoubtedly, however, it is the most important of the class in terms of comparison with theory (see below). In the most recent work based on OH detection, Kajimoto and coworkers¹⁰ have taken the first steps into stereodynamics by determining polarisation-sensitive Doppler profiles for certain product channels of the reactions with selected secondary and tertiary hydrocarbons. Essentially the only dynamical study not based on OH detection is the single determination by Suzuki and Hirota¹¹ of CH₃ umbrella mode vibrational state distributions from $O(^{3}P) + CH_{4}$ by diode laser absorption spectroscopy.

On the theoretical side, Luntz and Andresen¹² developed model pseudo-triatomic semi-empirical LEPS surfaces. Quasiclassical trajectory (QCT) calculations on these surfaces were successful in modelling the main qualitative features of their experimental results. Almost in parallel, Walch and Dunning¹¹ made the first rigorous *ab initio* prediction that $O(^{3}P) + CH_{4}$ proceeds via a preferred collinear O-H-C saddle-point geometry. This therefore supported the explanation arrived at independently by Luntz and Andresen¹² for the cold OH rotational distributions that are observed experimentally. Following some sparse intermediate work,^{14,15} there has been something of an explosion of theoretical interest in the $O(^{3}P) + CH_{4}$ system in recent years. Two separate fulldimensional ab initio potential energy surfaces (PESs) have been developed by Truhlar and coworkers¹⁶ and by González and coworkers.¹⁷ The Truhlar PES and its subsequent modifications¹⁸ have been exploited in reduced-dimensional quantum scattering calculations by the groups of Clary¹⁹⁻²² and Nyman.²³ These studies have focussed primarily on the influence of selective excitation of CH₄ vibrational modes on the reaction cross-section and product energy disposal. In parallel, González and coworkers^{17,24} have carried out QCT calculations on a pseudo-triatomic fit to their full-dimensional PES. They have been successful in reproducing the experimentally observed OH rotational state distribution,¹⁷ and more recently²⁴ have made predictions of various as yet unobserved features of the dynamics. Essentially all the theoretical work supports the original basic conclusion of a direct abstraction mechanism via a preferred collinear geometry.

In the current work we aim to extend the experimental knowledge base on this class of reactions in two ways. First, we use isotope substitution to provide confirmation of the nuclear framework dynamics of two representative reactions:

$$O(^{3}P) + CH_{4} \rightarrow OH + CH_{3}$$
(1a)

$$O(^{3}P) + CD_{4} \rightarrow OD + CD_{3}$$
(1b)

$$O(^{3}P) + cyclo-C_{6}H_{12} \rightarrow OH + cyclo-C_{6}H_{11}$$
 (2a)

$$O(^{3}P) + cyclo - C_{6}D_{12} \rightarrow OD + cyclo - C_{6}D_{11}$$
 (2b)

(where cyclo-C₆H₁₂ indicates cyclohexane). The energetics of the two reactions are represented in Fig. 1, which emphasises the lower barrier and greater exothermicity for abstraction from a secondary H-C bond in reaction (2). This is the first systematic investigation of isotope effects in these reactions and we shall consider whether the results agree with the accepted picture of the dynamics. It also provides valuable experimental corroboration of the OH product state partitioning for the parent $O(^{3}P) + CH_{4}$ reaction, (1a). As we have stressed above, this has only been reported once previously⁹ yet remains the benchmark for comparison with rigorous theory. The use of CD₄ eliminates a significant source of experimental interference as will be explained further below.

A second aim of the current work is to shed further light on electronic aspects of the reaction. It has been widely noted previously⁹ that the electronic fine-structure states of the openshell $OH(X^{2}\Pi)$ product are unequally populated. We have carried out a systematic study of this branching for both isotopomers of both reactions (1) and (2). This includes, for the

Probability

0.030

0.045

0.015

0.000

120

100

80

60

40

a peak at NO v = 0.



5.5

first time, a complete characterisation for both OH vibrational states produced in reaction (2). The intention is to establish whether the factors that determine the fine-structure state branching are independent of those controlling the nuclear framework rotation. This will provide a test of theoretical models²⁵ based on selective couplings between adiabatic electronic fine-structure surfaces. Although none of the rigorous theoretical work on $O(^{3}P) + CH_{4}$ has yet advanced to the treatment of multiple fine-structure surfaces, this general topic is currently the subject of intense theoretical^{26,27} and experimental²⁸⁻³¹ interest in related systems.

Experimental

The basis of the experimental method was essentially the same as that described previously,9 so only the main features are summarised here. The O(³P) atoms were generated by photolysis of NO₂ and the OH products probed by LIF. Experiments were carried out in a stainless steel vacuum chamber, constructed around a central six-way cross. The chamber was evacuated by a diffusion pump, backed by a rotary pump, with a base pressure of better than 1×10^{-6} Torr. During experimental runs, NO2 precursor and hydrocarbon reactant gases were flowed in via separate needle valves. This was designed to prevent their mixing prior to entering the chamber and minimise the undesired photolytic production of OH identified in several previous studies.⁵ In particular, it was successful in preventing isotope exchange between deuterium-labelled hydrocarbons and the contaminant responsible for the photolytic OH. We found virtually no measurable prompt OD signal. The total pressure in the chamber was controlled by partially throttling the diffusion pump. It was typically in the range 100-250 mTorr, made up of a 50:50 mixture of NO₂ and hydrocarbon reactant.

The photolysis and probe laser beams counter-propagated through the chamber. The entrance and exit arms were fitted with Brewster-angle windows and internal baffles to reduce scattered laser light. One of the main technical changes was that the photolysis light was provided by the 4th harmonic of a Nd:YAG laser (Continuum SLII-10) at 266 nm. Typical photolysis pulse energies were around 40 mJ.

In previous work⁹ we had used either shorter (248 nm) or longer (308 nm, 337 nm) excimer or N2 laser wavelengths. The implications of 266 nm photolysis for the collision energy distributions are shown in Fig. 1. These must necessarily be estimated because, as far as we are aware, there have been no direct measurements of the kinetic energy release for photolysis of NO₂ at this wavelength, nor indirectly of the internal state partitioning in the co-product NO. For the purposes of presentation in Fig. 1, we have assumed two scenarios for this NO distribution. In one, we have assumed that it is similar to that which has been measured³² at 248 nm, but curtailed by the reduction in the total energy available in the photolysis. The measured distribution at 248 nm apparently has a secondary maximum at NO v=0, corresponding to a component of relatively fast O(³P) atoms. This component is not observed at longer photolysis wavelengths in the same band.³³ Since it is not clear whether it would be present at 266 nm, we have also presented an alternative distribution in which a relatively low NO v = 0 population was imposed by extrapolating smoothly the populations in the higher levels. Having defined the NO vibrational populations, the corresponding centre-of-mass $O(^{3}P)$ + hydrocarbon collision energy distributions were obtained using standard expressions which account for the kinematics and the thermal motions of the NO2 precursor and hydrocarbon reactants.34

The tuneable probe laser light was provided by a Nd:YAGlaser pumped dye laser system (Spectron Laser Systems, SL803S + SL400G + SL400EX). It was not necessary to avoid optical saturation because of the comparative method used to

and

calibrate the effective linestrengths described below, so pulse energies up to 2–3 mJ were used to maximise LIF signals.

Fluorescence was collected by a short focal length fused silica lens mounted perpendicular to the mutual laser axis. There were several sources of undesired background signals. In addition to scattered light from the photolysis and probe laser beams, there was a strong photolysis-laser induced signal from the NO₂ precursor. This was most probably caused by an accidental double-resonance process in which vibrationally excited NO formed in the photolysis step was excited by absorption of a second 266 nm photon on the NO A-X (1.5) band. This resulted in strong emission on the NO A–X (1, v'') bands. The most inconvenient of these are the (1,8) and (1,9)bands that happen to fall in the same region as the OH diagonal bands. Two different methods were attempted to isolate the desired probe-laser induced fluorescence signal from the background signals. At the expense of lower throughput but with greater discrimination, the fluorescence was collimated and refocused on the entrance slit of a monochromator (Hilger and Watts, Monospek 1000, 1m focal length). Alternatively, more similar to our previous work⁹ but with a new custom filter designed to optimise discrimination between signal and background, the collimated light was passed through an interference filter before being refocused and detected.

In either case the transmitted light was detected by a photomultiplier tube and the signal captured by a transient digitiser (100 MHz, DSP 2001A). The digitiser was part of an integrated data-collection and control system (CAMAC, IEE 583) under the control of a microcomputer. The most important feature of this system was that it provided active control of the delay between photolysis and probe lasers, which could be cycled on a shotwise basis. This allowed, in particular, LIF excitation spectra for different delays to be recorded in parallel, as discussed further below.

Reactants and the precursor were used as supplied, other than the usual freeze-thaw cycling to removed dissolved air from liquid samples. The manufacturers and stated purities were NO₂ (BOC, 98.3%); CH₄ (BOC, 99.995%); CD₄ (Eurisotop, isotopic purity 99.99%); cyclo-C₆H₁₂ (BDH, 99%); cyclo-C₆D₁₂ (Goss, isotopic purity 99.5%).

Results

The primary raw data were LIF excitation spectra excited on the OH or OD -X off-diagonal (1,0) and (2,1) bands around 290 nm. Fluorescence was collected on the diagonal (1,1) and (2,2) bands in the region of 320 nm, isolated by either an interference filter or a monochromator. For the significantly populated ground-state N' levels, the corresponding levels accessed in the A ${}^{2}\Sigma^{+}$ state lie below the onset of predissociation for both vibrational levels of OD.35-38 For OH, although the A ${}^{2}\Sigma^{+} v = 1$ level state is unpredissociated below $N \sim 14$, all rotational levels of v = 2 are subject to predissociation. This means that the (2,1) band would not normally be considered ideal for determining OH ground state populations. The fluorescence quantum yield is reduced significantly and in an N-dependent fashion, varying by a factor of ~ 2 over the levels relevant to this study. However, because of the relative method we have used to calibrate the effective linestrengths (see below), this effect is automatically accounted for in the analysis. We therefore persisted with the OH (2,1) band because of the convenience of collecting spectra for OH v' = 1in the same region as the other product levels.

As noted above and seen in previous work,^{5,9} the photolysis laser generates a significant prompt OH concentration which partially obscures the desired reactive product from CH_4 and cyclo- C_6H_{12} . The photolytic contribution was eliminated operationally by recording a spectrum at a very short photolysis-probe delay of 50 ns in parallel with one at a slightly longer delay. The timing of the second spectrum was chosen to be as early as possible consistent with achieving adequate signal-to-noise. Values of 150 ns and 300 ns were used for cyclo- C_6H_{12} and CH₄, respectively, in conjunction with respective total pressures of 100 and 200 mTorr. In each case the 50 ns spectrum was subtracted from the later spectrum, leaving only the OH formed bimolecularly in the intervening period of 100 or 250 ns, respectively. As a check, spectra were recorded for cyclo- C_6H_{12} with the slightly higher pressures and longer delays used for CH₄. The OH populations were found to be not significantly degraded from their more assuredly nascent values at shorter times.

For OH(v' = 1), there was further interference from a LIF signal excited accidentally by the probe laser from nascent NO produced in the NO₂ photolysis. The NO B-X (0,7) and (0,8) bands partially obscure the longer wavelength region of the OH A-X (2,1) band, restricting the lines that could be used in the analysis.

In contrast, the OD LIF signal was found to be effectively free from any photolytic contributions. It was therefore sufficient for cyclo- C_6D_{12} and CD_4 to record spectra at respective photolysis-probe delays of 100 and 200 ns and total pressures of 100 and 250 mTorr. These contained essentially only reactively produced OD.

For both OH and OD, a further spectrum was recorded in parallel at a relatively long photolysis-probe delay of 20 µs. Examples of the typical time evolution of the OD LIF spectrum are shown for CD_4 and cyclo- C_6D_{12} in Fig. 2. We believe that under the long-time conditions, corresponding to several tens of gas-kinetic collisions, the OH or OD rotational distribution is essentially completely thermalised. The nascent distributions are generally not very substantially rotationally excited and therefore only a modest amount of rotational energy has to be transferred in collisions to achieve thermalisation. Rotational relaxation of OH is particularly efficient in collisions with polyatomic partners such as methane or cyclohexane, and so we believe several tens of gas-kinetic collisions will be more than adequate. We are confident that the majority of the OH has been present for a substantial fraction of the total delay time because the reactivity of the $O(^{3}P)$ atoms declines rapidly as they lose translational energy through collisions. The peak in the OH density, due to the balance between production and fly-out and other loss



Fig. 2 Representative time-evolution of OD A-X (1,0) LIF excitation spectra from the OD $\nu' = 0$ products of $O({}^{3}P) + CD_{4}$ (right panel, total pressure 400 mTorr) and $O({}^{3}P) + cyclo-C_{6}D_{12}$ (left panel, total pressure 80 mTorr). In each case, a sequence of three spectra are shown with photolysis-probe delays of 50 ns (lower trace), 200 ns (middle trace) and 20 µs (upper trace), respectively. The spectra have been artificially offset for the sake of clarity.

processes, is correspondingly observed at a time considerably earlier than that at which the thermal spectrum is measured.

Therefore, the ratio of prompt reactive to long-time thermal signals provides a method of calibrating the effective linestrengths as a function of N'. It eliminates the need to rely on calculated or previously measured linestrengths. No corrections are required for the wavelength dependence of the detection system in emission, differential optical saturation of lines with different linestrengths, differential rates of collisional quenching, and, in the case of OH A ${}^{2}\Sigma^{+} v = 2$, differential rates of predissociation (see above). Because of deliberate heavy optical saturation, the effect of any potential differential alignment of the nascent population relative to the isotropic thermal distribution would be substantially suppressed. In addition, because the spectra were recorded in parallel on an alternating shotwise basis, reactive product populations are automatically corrected for drifts in the experimental conditions such as photolysis and probe laser powers, gas composition and pressure, optical alignment, etc.

In practice, populations were extracted by using the program LIFBASE³⁸ to first simulate in the thermal spectrum the intensity of a particular line excited from a specific Λ -doublet, finestructure, rovibrational level of the X ² Π state. The intensity of the equivalent line in the reactive spectrum was then simulated by re-optimising the relevant population. The fractional thermal population is known straightforwardly from the Boltzmann distribution at room temperature. It may therefore be used with the ratio of populations in the two simulations to calculate a correctly calibrated relative population in the reactive spectrum. By repeating the process for different lines the relative reactive populations of the levels are built up. Statistics on the relative populations were obtained from at least four independent experimental runs and generally from several branches within each spectrum, depending on the chance blending of lines.

This comparative method happens to be particularly wellsuited to the $O({}^{3}P)$ + hydrocarbon reactions because of the characteristically cold rotational distributions. Our confidence in it is reinforced by the fact that the relative intensities of the lines in a single spectroscopic branch in the simulation generally agreed within $\sim 20\%$ with those in the experiment. Nevertheless, there was a practical limitation for the highest N' levels. Their fractional populations in the thermal spectra were too small to allow the intensities of the lines to be assessed reliably. For levels with N' > 8 and 12 in v' = 0 of OH and OD, respectively, we instead extrapolated the effective linestrengths established for the lower lines. The observed variation with N'depended on whether the monochromator or interference filter had been used to isolate the fluorescence, but was typically no more than 20% of the last thermally calibrated line. The interference filter data were more reliable for the higher N' lines because of the wider range of wavelengths detected in emission. The distributions we have reported here are therefore a synthesis of monochromator and filter data for lower N' lines, but exclusively filter data for the higher lines (which in any case represent a very small fraction of the total product yield).

Rotational distributions

The OH rotational distributions were found to be similar to those measured previously⁹ for CH₄ initiated by 248 nm photolysis of NO₂, and for cyclo-C₆H₁₂ with either longer or shorter photolysis wavelengths (or other methods of O(³P) production^{6,7}). Both OH $\nu' = 0$ and 1 were readily observed from cyclo-C₆H₁₂. Only OH $\nu' = 0$ could be detected for CH₄. We estimate from the level of baseline noise, and on the basis that previous measurements of the branching for cyclo-C₆H₁₂ are correct,^{6–8} that the upper limit on the branching ratio into OH $\nu' = 1$ from CH₄ is ≤ 0.03 .

More original are the OD distributions, which have not been investigated systematically for cyclo- C_6D_{12} and not at all for



Fig. 3 Distributions as a function of rotational quantum number, N', in the F₁ manifold of OD reaction products. $O(^{3}P) + CD_{4} \rightarrow OD v' = 0$ (circles); $O(^{3}P) + C_{6}D_{12} \rightarrow OD v' = 0$ (squares) and OD v' = 1 (triangles).

 CD_4 . Both OD v' = 0 and 1 are significantly populated for cyclo- C_6D_{12} . We did not search for OD v' = 2. For CD_4 , only OD v' = 0 is detectable at a level where rotational populations could be derived. However, there was a very weak OD v' = 1 signal that just exceeded the noise level, from which we estimate on the same assumption as above that the branching into OD v' = 1 for CD_4 is ~0.06.

Fig. 3 illustrates the distributions over N' for the F_1 component of OD in the significantly populated product levels. The features of the OD rotational distributions mirror those seen previously⁵ for CH₄ and cyclo-C₆H₁₂. The OD v'=0 distribution is significantly hotter for CD₄ than for cyclo-C₆D₁₂. For cyclo-C₆D₁₂ itself, the rotational distribution is substantially colder in v'=1 than in v'=0.

The average characteristics of the various OH and OD distributions are collected in Table 1, reflecting the qualitative comments above. The uncertainties quoted only include the statistical estimate of the precision and not the accuracy as it might be influenced by systematic factors in the method of extracting populations. For the sake of later discussion, in each case we have equated the average energy in rotation to that of a Boltzmann distribution. This allows the assignment of a corresponding apparent temperature. We do not, of course, expect a Boltzmann distribution to be a perfect description of a dynamically produced population. If Boltzmann plots are constructed they are indeed moderately non-

Table 1 Average energies in rotation, $\langle E_{rot} \rangle$, and equivalent Boltzmann temperatures, T_{rot} , for observed OH and OD product vibrational levels

Reaction	Product level	$\langle E_{\rm rot} \rangle / {\rm cm}^{-1a}$	$T_{\rm rot}/{ m K}^{a}$
$O({}^{3}P) + CH_{4}$ $O({}^{3}P) + CD_{4}$ $O({}^{3}P) + cyclo - C_{6}H_{12}$	OH $v' = 0$ OD $v' = 0$ OH $v' = 0$ OH $v' = 1$	$\begin{array}{c} 322 \pm 32^{b} \\ 391 \pm 46^{b} \\ 260 \pm 12 \\ 137 \pm 12 \end{array}$	$\begin{array}{c} 464 \pm 48^{b} \\ 563 \pm 68^{b} \\ 376 \pm 18 \\ 197 \pm 18 \end{array}$
$O(^{\circ}P) + \text{cyclo}-C_6D_{12}$	$\begin{array}{l} \text{OD } v' = 0 \\ \text{OD } v' = 1 \end{array}$	$\begin{array}{c} 241\pm8\\ 139\pm6\end{array}$	$\begin{array}{c} 347\pm12\\ 200\pm8 \end{array}$

^{*a*} Quoted uncertainties represent 2σ error limits (95% confidence intervals) of the mean evaluated purely from the statistical variation in at least four independent measurements. They do not include any estimate of systematic uncertainties, which may exceed the statistical scatter as discussed in the text. ^{*b*} Values for OH and OD v' = 0 from CH₄ and CD₄, respectively, may have been slightly reduced by an inability to observe populations in the next N' level above the last observed level due to spectroscopic blending.

Although the qualitative trends with reactant and product vibrational level are the same, we systematically find somewhat lower absolute average energies in rotation for the OH products than in our previous work.⁹ We doubt that any differences are necessarily connected with changes in the photolysis wavelength to 266 nm. It is more likely that they are related to different procedures used to extract populations from the raw data.

More significant are the comparisons between OH and OD within this study, where a common photolysis wavelength and method of analysis were used. A very clear result is that the rotational *energy* release is very similar for the OH and OD products in a given vibrational level for a particular reactant. This is reflected in the average values in Table 1. The agreement is particularly convincing for cyclohexane, but we note that there is a slight additional uncertainty in the averages for CH₄ and CD₄ because of spectroscopic blending of lines for the next N' above the last observed level. Probably more striking is the similarity of the distributions themselves. The effect is illustrated in Fig. 4, where the various $F_1(N')$ distributions are plotted as a function of rotational energy.

Fine-structure distributions

As is very well known and has been widely discussed in this and many other contexts, the open-shell nature of the X ${}^{2}\Pi$ ground state of OH gives rise to two manifolds of rotational levels, labelled F₁ and F₂. At low values of N' the angular momentum coupling most closely approximates to Hund's case (a). In this limit the F₁ and F₂ manifolds correspond to the $\Omega = 3/2$ and 1/2 spin-orbit components, respectively. The F₁ state lies lower in energy. The splitting for the lowest level, N' = 1, is around 125 cm⁻¹ for OH,³⁹ and only slightly higher (131 cm⁻¹) for OD.⁴⁰ With increasing N' there is a progression



Fig. 4 Product state distributions as a function of rotational energy in the F_1 manifold. Distributions have been normalised to have the same area. Lower panel: OH and OD v' = 0. $O(^3P)$ reaction with CH₄ (open circles), CD₄ (filled circles), cyclo-C₆H₁₂ (open squares) and cyclo-C₆D₁₂ (filled squares). Upper panel: OH and OD v' = 1. $O(^3P)$ reaction with cyclo-C₆H₁₂ (open triangles) and cyclo-C₆D₁₂ (filled triangles).



Fig. 5 Collected OH and OD fine-structure state ratios for both isotopes and all observed product vibrational levels of reactions (1) and (2). Identifying symbols as in Fig. 4.

towards Hund's case (b), which would eventually lead to the association of F_1 and F_2 labels with levels split by the spin-rotation interaction.

We have re-measured for confirmation purposes the F_1/F_2 ratio reported several times previously⁶⁻⁹ for OH $\nu' = 0$ from cyclo-C₆H₁₂. Importantly, the N'-dependence of this ratio for OH $\nu' = 1$ was further examined, expanding on the limited previous data.⁶ Similarly, the single previously undeveloped result⁶ for OD $\nu' = 0$ from cyclo-C₆D₁₂ was extended, and the first data for OD $\nu' = 1$ obtained for this reactant. The measurements are more challenging for the methane substrates because of the poorer signal-to-noise. Nevertheless, we have obtained confirmation of our single previous measurement⁹ of the ratio for OH $\nu' = 0$ from CH₄, and the first results of this kind for OD $\nu' = 0$ from CD₄.

The results of this fairly extensive survey of the F_1/F_2 ratios are collected in Fig. 5. The most striking feature is that, within the statistical scatter, there is a general commonality of behaviour. In all cases there is preference for the lower-lying F_1 component that declines steadily with N'. A similar trend had been seen previously for the OH v' = 0 products from various hydrocarbons,⁵ but is now confirmed to extend to the higher product vibrational level and to be essentially independent of hydrogen isotope.

A-doublet populations

Each of the OH rotational levels within each spin-orbit manifold is further split by Λ -doubling. The two components have respective A' and A" reflection symmetries. In the limit of high rotation, they correspond to the unpaired π -electron density being in, or perpendicular to, the plane of rotation.

We have investigated the Λ -doublet ratios for different product levels of the various reactants. This is illustrated in Fig. 6 for the F₁(N') components. The F₂ results are similar but more scattered. This is partly because of the poorer signal-to-noise associated with the lower F₂ populations, but also because both the OH and OD (1,0) Q₂ branches happen to be extensively blended. In no case was a systematic deviation from unity identified, also agreeing with the previously available results.⁵

Discussion

Rotational energy distributions

The aim of confirming the trends in the OH mechanical rotational distributions through isotopic substitution has been



Fig. 6 Collected OH and OD Λ -doublet ratios in the F₁ manifold for both isotopes and all observed product vibrational levels of reactions (1) and (2). Identifying symbols as in Figs. 4 and 5.

successfully achieved. The OD distributions reproduce the qualitative features of those for OH which have been more widely measured⁵ for the higher hydrocarbons, but, as we have stressed, only once previously⁹ for the parent compound CH₄. The distributions are all characteristically cold, but with noticeably more rotational energy release into OD v' = 0 for CD₄ than for cyclo-C₆D₁₂. This is despite the converse trend in the exothermicity, as shown in Fig. 1. The same effect for OH products has been interpreted previously as a stereo-dynamical effect,⁹ related to a wider cone of acceptance for abstraction of a hydrogen atom from the sterically less-crowded methane molecule. The trend towards lower rotational energy release in the higher vibrational level seen previously^{6–9} for normal cyclo-C₆H₁₂ is also reproduced in the results for cyclo-C₆D₁₂.

Our principal new quantitative result on the rotational branching is that the absolute rotational energy release is almost independent of isotope for a given reactant and hydroxyl product vibrational level. The average values in Table 1 and especially the distributions in Fig. 4 illustrate this point. To a reasonable approximation it will also be true that the fraction of the available energy being converted to hydroxyl rotation is similarly independent of isotope. Isotopic substitution has only a modest kinematic effect on the centre-of-mass collision energy. Its effects on the reaction exothermicity are also quite small relative to the average energy of reactants crossing the barrier, as shown in Fig. 1. This shift is largest for v' = 1 products (only characterised from cyclohexane), but this appears not to perturb significantly the rotational energy release.

It is interesting to consider how this new information on isotope effects reflects on the accepted mechanism for the $O(^{3}P)$ + hydrocarbon reactions. As noted in the Introduction, the characteristically cold rotational distributions have been interpreted as strong evidence for an abstraction mechanism through predominantly collinear geometries. Among other things, the observed lack of an experimental OH Λ -doublet preference is also consistent with this conclusion. All levels of ab initio calculation support such a preferred geometry. The most recent theoretical examination of the nuclear dynamics is that of González and coworkers,²⁴ who have expanded on previous discussions.^{5,10,17} They used a QCT approach on a model O-H-(CH₃) pseudo-triatomic surface deduced from their full-dimensional ab initio electronic structure calculations. From the point of view of predicting the likely effects of isotopic substitution on rotational energy release, the most critical feature of their analysis is the interplay between impact parameter, the geometry at the classical turning point, angular scattering, and OH rotational motion.

What González and coworkers find²⁴ is that trajectories may be divided roughly into two categories of "rebound" and "non-rebound". The rebound trajectories, as the name suggests, are predominantly back-scattered. This can be traced to a tendency towards low impact parameters. As a consequence, a high proportion of the initial translational energy may be used to penetrate into repulsive regions of the potential. This allows closer approach of the reactants and, more crucially, reaction through energetically less favoured bent geometries. The bending angle creates a torque during the impulsive separation of the products that ultimately causes OH rotation. In contrast, the non-rebound trajectories have characteristically higher impact parameters, which makes them less efficient in converting translational to potential energy. They reach less repulsive regions of the potential, producing less rotationally excited OH that is more forward scattered.

González and coworkers' calculations²⁴ suggest that the non-rebound trajectories only contribute significantly at relatively high collision energies. At our typical experimental energies, they predict that rebound trajectories would be strongly dominant. On this basis, we now present a simplified analysis of the effects of isotopic substitution on the assumption that OH rotation derives entirely from impulsive energy release *via* a modestly bent geometry, to see if it is consistent with the experimental observations.

In this limit, the initial recoil velocity, $v_{\rm H}$, imparted to the hydrogen atom as it is repelled by the radical fragment, R, is simply derived from energy and linear momentum conservation:

$$v_{\rm H} = \left(\frac{2m_{\rm R}E}{m_{\rm H}m_{\rm HR}}\right)^{1/2} \tag{3}$$

E is the energy being released repulsively and m_i are the masses of the various fragments. Since $m_R/m_{HR} \approx 1$, it can be seen that the hydrogen atom velocity is approximately inversely proportional to the square root of the mass of the isotope involved.

The rotational angular momentum that this generates as the H atom attaches to the O atom is

$$j_{\rm OH} = \mu_{\rm OH} v_{\rm H} b_{\rm eff} = \frac{m_{\rm H} m_{\rm O}}{m_{\rm OH}} \left(\frac{2m_{\rm R} E}{m_{\rm H} m_{\rm HR}}\right)^{1/2} b_{\rm eff}$$
 (4)

where $b_{\rm eff}$ is an effective impact parameter or lever arm that depends only on the O–H–R angle. Given that $m_{\rm O}/m_{\rm OH}$ is also ~ 1 , the OH angular momentum is approximately directly proportional to the square root of the mass of the hydrogen isotope.

Finally, the OH rotational energy is

$$E_{\rm OH}^{\rm rot} - \frac{\dot{j}_{\rm OH}^2}{2\mu_{\rm OH}r_{\rm OH}^2} = \frac{m_{\rm O}m_{\rm R}}{m_{\rm OH}m_{\rm HR}} \left(\frac{Eb_{\rm eff}^2}{r_{\rm OH}^2}\right)$$
(5)

where r_{OH} is the OH bond length. The approximately linear dependence of both j_{OH}^2 and μ_{OH} on m_H leads to a rotational energy that is approximately *independent* of the mass of the hydrogen atom. Taking the specific case of O+CH₄ versus O+CD₄ (and noting that the mass of the R fragment also changes slightly because of the substitution of the non-reactive hydrogen atoms), eqn. (5) predicts that the OH rotational energy should be only 10% higher than for OD. This figure is even smaller at 7% for the O+cyclo-C₆H₁₂ and C₆D₁₂ pair.

We conclude therefore that an impulsive abstraction mechanism *does* appear at least qualitatively consistent with our experimental observation of a lack of a significant dependence of the hydroxy rotational energy on hydrogen isotope. Admittedly we have used a rather crude model and it would be desirable to test this conclusion more rigorously through scattering calculations on the available potential surfaces. Although Palma and Clary^{22} have included $O(^{3}P) + CD_{4}$ in their latest reduced dimensional quantum scattering calculations, their treatment did not include a prediction of product rotational partitioning. There are also currently no classical trajectory results available for CD_{4} . It would be an interesting test to see if the relatively successful prediction¹⁷ of the OH rotational distribution for normal CH₄ could be repeated for CD_{4} on the González and coworkers surface.

Clearly, identifying that the OH and OD rotational distributions are equivalent in terms of energy amounts to saying that they are *not* the same in terms of angular momentum. There are therefore other conceivable mechanisms in which the OH rotation would not be independent of isotope, but which are excluded by the observations. For example, a stripping mechanism in which the OH rotation derived primarily from conversion of a fixed proportion of reactant orbital angular momentum, l, to product rotation, j, would fall into this category.

It has been noted previously that the $O(^{3}P)$ + hydrocarbon reactions share a close resemblance with some aspects of the corresponding $Cl(^{2}P) + hydrocarbon$ reactions.^{9,10} Substantially more dynamical insight has been gained into the Cl(²P) reactions, as detailed in a recent review by Valentini.⁴¹ For reaction with the vibrational ground state of methane, the mechanism has been concluded^{41,42} to be direct abstraction *via* relatively low-impact parameter collisions with near-collinear geometries. This is clearly reminiscent of the mechanism proposed above for $O(^{3}P) + CH_{4}$. The effects of isotopic substitution on the rotational distributions of the HCl and DCl products of $Cl(^{2}P) + CH_{4}$ and CD_{4} have also been measured.⁴² Reassuringly, the HCl and DCl absolute rotational energies are also very similar, further consistent with similar abstraction mechanisms operating for $Cl(^{2}P)$ and $O(^{3}P)$ with methane. We note also that the $Cl(^2P)$ studies^{30,43} have uncovered a contribution to reaction from thermally excited bending and torsion vibrational states. This cannot be excluded as a possibility in the current studies on O(³P) reactions, particularly since reduced dimensional quantum scattering calculations¹⁹⁻²³ predict strong vibrational enhancements for $O(^{3}P) + CH_{4}$.

Fine-structure state partitioning

As in previous work on hydrocarbons containing normal hydrogen,⁵ we see a clear preference for the F_1 fine-structure state of the OH product. This is confirmed systematically for the first time to apply to OD products from deuterated hydrocarbons. The quality of the data for cyclohexane is also significantly improved. This allows a confident identification of a systematic decline with N' in the F_1/F_2 ratio, for both OH and OD, even after the correction for the different spatial degeneracies of F_1 and F_2 levels sharing the same N' has been applied. The data are presented in this form in Fig. 7.

A principal question we are attempting to address is whether the fine-structure state partitioning is a reflection of the same factors as those that govern the product nuclear framework rotation. If these were the same factors, a particular product level should receive its share of the population only on the basis of its energy and degeneracy, independent of spin–orbit manifold. Because, as discussed above, the OH and OD rotational energy release are almost identical for a given vibrational manifold, the observed similarity of the OH and OD fine-structure state partitioning does not happen to help resolve this question.

Much more incisive is a careful comparison of the finestructure state partitioning in the different product vibrational levels. The rotational distributions in OH and OD v' = 1 are *much colder* than those in v' = 0 (see Fig. 4 and Table 1). However, the fine-structure state partitioning in all of these levels is essentially the *same* (Fig. 5). We attempt to illustrate in



Fig. 7 Degeneracy-weighted OH and OD fine-structure state distributions from $O(^3P) + cyclohexane$, reaction (2). Lower panel: OH and OD v' = 0; cyclo-C₆H₁₂ (open squares) and cyclo-C₆D₁₂ (filled squares). Upper panel: OH and OD v' = 1; cyclo-C₆H₁₂ (open triangles) and cyclo-C₆D₁₂ (filled triangles). In both panels, the experimental results (with error bars) are joined by solid lines. Predictions on the basis of equivalent Boltzmann rotational temperatures, as discussed in the text, are joined by dotted lines.

Fig. 7 how different the observed F_1/F_2 ratios are from those that would have been observed if they had been simply a facet of the overall mechanical rotational energy release. As discussed above, each of the experimental product rotational distributions is reasonably well characterised by an equivalent Boltzmann temperature (Table 1). The F_1/F_2 ratios that would be expected on the basis of these temperatures have been included in Fig. 7. For OH and OD v' = 0 products, the predicted F_1/F_2 ratios moderately exceed the observed values. In contrast, for v' = 1 the predicted ratio is much too high, lying well beyond any experimental uncertainty.

We conclude therefore that the product spin–orbit branching is clearly *decoupled* from the factors that determine the deposition of mechanical rotational energy. This lends support to the proposition that this branching is a truly electronic effect, with a potential explanation lying in the coupling of adiabatic electronic surfaces. This idea was first proposed in the original work of Andresen and Luntz,⁶ but has subsequently been refined and developed.²⁵

The essence of the later models²⁵ is summarised in Fig. 8. A collinear geometry is assumed, justified by the low levels of rotational energy release as discussed above. The entrance channel surfaces correlate with the distinct $O({}^{3}P_{j})$ fine-structure states. Only the degenerate ${}^{3}\Pi$ surface is reactive, with the ${}^{3}\Sigma^{-}$ surface corresponding to an unfavourable orientation of a filled p-orbital towards the hydrocarbon. The OH product fine-structure surfaces similarly correlate with the reactive ${}^{3}\Pi$ surface and an unreactive ${}^{1}\Pi$ surface. The product state partitioning is predicted by projecting the flow of population from the initial $O({}^{3}P_{j})$ states through intermediate surfaces to the OH products.

As we have shown previously,²⁵ the prediction on the assumption of purely adiabatic behaviour is in poor agreement with experiment. Consequently, we examined the probability



Fig. 8 Fine-structure correlations in the reaction of $O({}^{3}P)$ with a hydrocarbon (assumed cylindrically symmetric) *via* a collinear geometry. Upper panel: fully adiabatic correlations. Lower panel: partially non-adiabatic correlations, with mixing of surfaces (indicated by broken lines) which have the same parity and projection of total electronic angular momentum, Ω .

of kinetically induced coupling of the surfaces. There was independent information available on the coupling strengths of entrance-channel surfaces from magnetically selected molecular beam scattering measurements of total elastic cross-sections.⁴⁴ There was also evidence of consistent propensity rules in *j*-changing inelastic collisions.⁴⁵ On this basis we proposed²⁵ that there should be effectively complete non-adiabatic mixing of populations on surfaces sharing the same parity and value of Ω , the projection of the total electronic angular momentum onto the collinear axis.

Adopting the available experimental values^{46,47} of the initial $O({}^{3}P_{i})$ populations from NO₂ photolysis in the relevant electronic band (which, if anything, should apply better at 266 nm where they were measured⁴⁶), we predicted²⁵ an OH F_1/F_2 ratio of 1.72. This is encouragingly comparable to, although exceedingly slightly on average, the limiting low N' degeneracy-corrected values for different product vibrational levels and isotopomers of cyclohexane in the new results in Fig. 7. The similar values for different product vibrational levels, as observed experimentally, is also compatible with the model because it does not distinguish between them. Furthermore, none of the assumptions in the model would suggest that OH and OD should differ, at least in the limit of rotationless products. As we have discussed previously,²⁵ it is reasonable that the predictions of the model should be most valid in the low N' limit. Among the reasons are the progression from Hund's case (a) to (b) coupling with increasing N' in the OH product, with corresponding decoupling of the spin from the molecular axis. The basic assumption of collinear approach also breaks down increasingly if it is correct that the higher N'products are associated with more bent geometries, as supported by the analysis of González and coworkers²⁴ discussed above. The use of the degeneracy-correcting weighting factor is also invalid if the products are significantly aligned and therefore don't span all m_J levels equally. On dynamical grounds this is more probable as product rotation increases, although it is also true that the degeneracy correction then becomes less significant.

Caution should clearly be exercised not to over-interpret the apparent success of the model because it has still only been possible to compare it against what is essentially a single experimental observation. The question of whether this really reflects a residual memory of the entrance channel populations would be more incisively tested if these could be varied independently. That has not yet been achieved experimentally. As has been discussed recently by Brouard and coworkers,48 there are other reactions, such as $H + N_2O$, H_2O and CO_2 , for which there are no fine-structure splittings in the entrance channel but which nevertheless produce a similar F1 preference in the OH product. These must, by definition, be controlled by exit-channel effects. Brouard et al. deduce⁴⁸ that the results imply partially non-adiabatic behaviour, lying between fully adiabatic and fully scrambled (suddenly recoupled⁴⁹) limits. We therefore thoroughly agree that a single observation of product fine-structure state partitioning is not a very incisive indicator of entrance channel mixing. Nevertheless, if partially non-adiabatic behaviour is observed in the exit channel of reactions for which it is excluded in the entrance channel, it is reasonable to expect that it may take place in both entrance and exit channels for reactions where both possibilities exist. This is just the case for the $O({}^{3}P)$ + hydrocarbon reactions, as has been included in our model.²⁵ A theoretical resolution of this question for systems such as $O(^{3}P) + CH_{4}$ may well have to wait for future developments of the rigorous ab initio methods just beginning to be applied to model three atom systems such as Cl and $F+H_2.^{26,27}$

Conclusions

New dynamical experimental results have been obtained for the reaction of $O(^{3}P)$ + deuterium-substituted hydrocarbons CD_{4} and cyclo- $C_{6}D_{12}$. These have successfully confirmed the main features of hydroxyl radical rotational energy release observed here, and previously, for normal hydrogen compounds.

The rotational *energy* release is found to be essentially independent of the hydrogen isotope for all observed OH and OD product levels of both reactions. This fits in with the accepted mechanism for the reaction involving a direct, nearcollinear abstraction, with the product rotation determined primarily by the geometry at the point of repulsive energy release.

The fine-structure state partitioning is found to be independent of isotope and, significantly, of OH or OD product vibrational level. This implies that the determination of finestructure populations is decoupled from the factors controlling mechanical rotational energy release. It appears consistent with a previously derived model that includes selected nonadiabatic couplings between adiabatic fine-structure surfaces.

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