

## FEATURE ARTICLE

## Role of Hydrogen-Bonded Intermediates in the Bimolecular Reactions of the Hydroxyl Radical

Ian W. M. Smith<sup>\*,†</sup> and A. R. Ravishankara<sup>‡</sup>

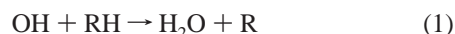
School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2 TT, U.K., National Oceanic and Atmospheric Administration, Aeronomy Laboratory, 325 Broadway, Boulder, Colorado 80303, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

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Because of their importance in atmospheric and combustion chemistry, the rate coefficients and mechanisms of gas-phase reactions of the OH radical have been studied extensively, and the kinetic database for these reactions is unsurpassed. The OH radical has a rather large electric dipole moment (1.668 D) and is clearly capable of forming strong hydrogen bonds. In this article, we examine the evidence for the importance of such interactions in reactions of OH. We propose that the reactions of OH with alkanes and with HNO<sub>3</sub> represent extremes of behavior, with no effect of hydrogen bonding in the first case but reaction via a rather strongly bound intermediate complex in the second. From this base, we go on to discuss, in turn, the reactions of OH with carboxylic acids, aldehydes, ketones, hydrogen halides, and CO, with the emphasis on the possible role of hydrogen bonding between the reagents of these reactions.

## 1. Introduction

Mainly because of their importance in the chemistry of the Earth's atmosphere,<sup>1</sup> the reactions of the hydroxyl radical have been studied very intensively over the past 30 years. The great majority of bimolecular reactions between OH radicals and *molecular*, as distinct from *radical*, co-reagents occur by H-atom transfer, that is, the hydroxyl radical extracts a H atom from the molecular reagent to form a molecule of water and a new radical:



Such reactions are mainly responsible for initiating the oxidation of a vast majority of hydrogen-containing species in the atmosphere. Because of the need for data that can be used in atmospheric models, many of these reactions of OH have been studied at least over the ranges of temperature and total pressure that are found in the atmosphere (ca. 190–310 K and 1–760 Torr). Although the current uncertainty in measured rate constants varies from reaction to reaction, the overall quality and range of the kinetic database for reactions of OH radicals is second to none.<sup>2,3</sup> These kinetic measurements, especially those at low temperatures, have been important in discovering new and interesting phenomena.

In this article, we examine the evidence that, in a number of reactions of the OH radical, forces resulting from hydrogen bonds between OH and the co-reagent affect the collision

dynamics and hence the kinetics of reaction. At the outset, we distinguish between, on one hand, species that arise when OH radicals add to an electron-rich moiety, such as molecules containing double (or triple) chemical bonds or an aromatic ring, in which case a rather strongly bound adduct is formed, and, on the other hand, the more weakly bound complexes that result from the formation of hydrogen bonds. Under suitable conditions, the former can be observed, and they can be thought of and dealt with as true reaction intermediates. Except under extreme conditions, such as those generated in supersonic expansions, the latter more weakly bound complexes can be too short-lived to be detected easily, but their existence can be inferred by the way in which they affect the overall behavior of a reaction. We are concerned in this article with the latter, moderately bound adducts.

The dipole moment of the OH radical is well-established as 1.668 D.<sup>4</sup> This value is similar to that of HF (1.826 D),<sup>4</sup> so it is reasonable to suppose that OH might form hydrogen bonds that are comparable in strength with those involving HF. Because OH is a highly reactive free radical and any complex that OH forms might dissociate very rapidly to reaction products, there have been rather few experimental studies of its weakly bound complexes. However, in the case of the analogous HF complexes where dissociation to products is not energetically feasible, there have been many experiments utilizing rotational<sup>5</sup> and vibrational<sup>6</sup> spectroscopy, including some in which the other species in the complex is a molecule that can undergo reaction with OH. The information gleaned from these experiments can be used to estimate the dissociation energy and structure of any similar complex formed by OH.

In considering the influence of hydrogen-bonded complexes on the kinetics of reactions of the OH radical, two extremes of

\* Corresponding author. E-mail: iwmsmith@bham.ac.uk. Fax: +44 121 414 4426.

<sup>†</sup> The University of Birmingham.

<sup>‡</sup> National Oceanic and Atmospheric Administration and Department of Chemistry and Biochemistry.

behavior can be identified. The first is the case in which reactive collisions occur directly, and any hydrogen-bonded forces, if they exist, exert no significant influence on the collision dynamics. At the other extreme, a hydrogen-bonded complex can be formed with an overall bond strength that appreciably exceeds  $k_B T$  at the temperature of the experiments. In this situation, a complex of appreciable lifetime may form before it dissociates to products, redissociates to reagents, or is stabilized by collisions. Even the stabilized complex can lead to products. An intermediate type of behavior is also possible where no collision complex is formed, but the forces due to hydrogen bonds are sufficient to influence the collision dynamics as the reagents approach. Such forces may, for example, orient the reagents favorably or unfavorably for reaction. In either case, such forces will exert the most influence on reagents when they are in low rotational states. Consequently, the rotationally specific rate constants may depend significantly on the rotational states of the reagents, and the thermal rate constants, especially at low temperatures, will be influenced by the different values of the rotationally state-specific rate constants and the temperature-dependent distribution of reagents over their rotational levels.<sup>7</sup>

In this article, the emphasis is on *experimental* evidence that points to the influence of hydrogen-bonded complexes or the forces resulting from hydrogen bonds, on the behavior of reactions of OH radicals. However, where they are available, we have incorporated the results of *ab initio* calculations that have explored how the potential energy varies along the minimum energy path for the reactions that we consider. We invoke four types of experimental evidence, although data of all these kinds are available only for a few systems. First and foremost, an unusual dependence of the rate constant for a reaction on temperature and total pressure can indicate that a reaction proceeds through a short-lived complex, possibly one held together by hydrogen bonds. The reaction between OH radicals and HNO<sub>3</sub> (see below, section 2.b.) is the prototype for such unusual behavior.

The participation of at least two H atoms in the reactions represented by eq 1 allows both primary and secondary kinetic isotope effects<sup>8</sup> to be examined via D for H atom substitution, either in the molecular reagent or in the OH radical. Examination of the magnitude of these effects, the *primary* effect, where one compares the rate constants for OH (or OD) reacting with RH and RD, and the *secondary* effect, where one compares the rate constants for OH and OD reacting with RH (or RD), is one way in which clues can be obtained as to whether a given reaction proceeds *directly* or via a hydrogen-bonded (or other) adduct of significant lifetime. The observation of an appreciable primary kinetic isotope effect must, however, be interpreted with caution. In a direct reaction, such an effect is generally explained in terms of transition-state theory. In particular, substitution of D for H can increase  $\Delta E_0^\ddagger$ , the difference in energy between the zero-point levels in the transition state and in the separated reagents, and hence lower the rate constant for reaction. On the other hand, in a reaction proceeding via a complex, a strong isotope effect may arise if a significant barrier separates the complex from the products. In this situation, an H atom will tunnel through the barrier faster than a D atom.

In addition, it makes sense to compare the rate constants for reactions of OH radicals with those for the corresponding reactions of Cl atoms, namely,



where the possibility of hydrogen bonds between the reagents

does not exist. One might suppose that Cl atoms would react more slowly with a given RH molecule than would OH because the H—Cl bond is weaker than the H—OH bond, with the result that reaction 2 is less exothermic than the corresponding reaction 1. However, this expectation is contrary to what is often found.<sup>2,3</sup> In a series of papers, Donahue and co-workers<sup>9,10</sup> have argued that the barrier to direct H-atom transfer reactions is the result of an avoided crossing between two diabatic states, one that correlates with the neutral reagents and ionic products and the other, with ionic reagents and the neutral products of reaction. In this model, which is discussed further in section 2.a. on the reactions of OH with alkanes, the barriers for reactions of Cl atoms are less than those for the corresponding reactions of OH chiefly because of the higher electron affinity of Cl (3.61 eV) compared with that of OH (1.83 eV).<sup>4</sup> Within this framework, if a given molecule reacts faster with OH than with Cl, it suggests that the OH reaction may occur by other than a direct abstraction mechanism, probably one involving the participation of a hydrogen-bonded complex.

Finally, an unusually rapid rate of vibrational relaxation of OH by a molecular reagent may point to the formation of collision complexes that facilitate energy transfer,<sup>11</sup> though once again one must carefully assess the possibility of other explanations for such large experimental values.

The present review is structured as follows. We begin by considering two cases: (i) the reactions of OH with alkanes, especially OH + CH<sub>4</sub>, in which it seems safe to assume that hydrogen-bonding plays no role and (ii) the reaction of OH with HNO<sub>3</sub>, where there is now a substantial body of evidence that reaction proceeds through a hydrogen-bonded adduct of significant lifetime. Having considered these two prototypes at the extreme ends of the behavior that we have described, we consider the experimental and theoretical evidence for the influence of hydrogen bonding in a number of other reactions of OH: with carboxylic acids, with ketones and aldehydes, with hydrogen halides, and finally with CO, a bimolecular reaction of OH that is almost unique in that it does not proceed by H-atom transfer but rather by O-atom transfer via a HOCO intermediate. We begin by briefly considering the reactions of OH radicals with alkanes.

## 2.a. Reactions of OH with Alkanes, Especially with CH<sub>4</sub>

In the atmosphere, the reactions of OH with alkanes initiate their oxidation and therefore largely control the atmospheric lifetimes of these species.<sup>12</sup> Consequently, these reactions, especially that of OH with CH<sub>4</sub>, have been extensively studied.<sup>2,3,13</sup> Lester and co-workers have studied the weakly bound complex between OH radicals and CH<sub>4</sub>.<sup>14,15</sup> The equilibrium structure has the H atom of OH pointing toward the C atom of CH<sub>4</sub> between three of the C—H bonds and along the line of the fourth C—H bond so that O—H...C—H is linear. The dissociation energy of this complex is equivalent to  $D_0 = 210 \pm 20 \text{ cm}^{-1}$ . This value is not significantly different from that which would be expected on the basis of dipole-induced dipole plus dispersion forces. It is also much smaller than both the average thermal energy associated with CH<sub>4</sub>/OH collision pairs at  $T \geq 200 \text{ K}$  and the barrier to reaction inferred from the activation energy given in Table 1.

All the evidence points to the reactions of OH with alkanes, especially methane, taking place directly over a potential energy surface with a significant barrier but no well that exerts a significant effect on the collision dynamics. There is no evidence that the rates of any of these reactions depend on total pressure. Of course, as with other H-atom transfer reactions, it is possible that tunneling is a significant factor in these reactions.

**TABLE 1: Comparison of Rate Constants ( $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and Activation Energy ( $(E_a/R)/\text{K}$ ) at 298 K for the Reactions of OH and Cl with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CD}_4$ ,  $\text{C}_2\text{D}_6$ , and  $\text{C}_3\text{D}_8$ <sup>a</sup>**

reagent	OH	Cl
$\text{CH}_4$	$6.3 \times 10^{-15}$ ( $1775 \pm 100$ )	$1.0 \times 10^{-13}$ ( $1400 \pm 150$ )
$\text{C}_2\text{H}_6$	$2.4 \times 10^{-13}$ ( $1070 \pm 100$ )	$5.7 \times 10^{-11}$ ( $90 \pm 90$ )
$\text{C}_3\text{H}_8$	$1.1 \times 10^{-12}$ ( $600 \pm 100$ )	$1.4 \times 10^{-10}$ ( $-40 \pm 250$ )
$\text{CD}_4$	$8.7 \times 10^{-16}$ ( $2100 \pm 200$ )	$8.5 \times 10^{-15}$ ( $2150 \pm 100$ )
$\text{OD} + \text{CH}_4$	$6.8 \times 10^{-15}$ ( $1640 \pm 40$ )	
$\text{C}_2\text{D}_6$	$5.7 \times 10^{-14}$ ( $1425$ )	$1.9 \times 10^{-11}$ ( $380 \pm 70$ )
$\text{C}_3\text{D}_8$	$4.0 \times 10^{-13}$ ( $770$ )	

<sup>a</sup> Most of the data in this Table comes from the evaluations performed by the IUPAC and NASA panels.<sup>2,3</sup> Data for most of the deuterated species comes from the laboratory of one of the present authors. The activation energies are appropriate for a rather small temperature range around 298 K, and curvature in the Arrhenius plots is ignored.

Table 1 compares the rate constants for the reactions of OH with the three simplest alkanes,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ , both with one another and with the rate constants for the corresponding reactions of Cl atoms. Two conclusions stand out. First, the overall rate constants for the reactions of both OH and Cl increase sharply as one proceeds along the alkane series, leading to considerably reduced atmospheric lifetimes for the higher alkanes relative to that for  $\text{CH}_4$ . Second, the rate constants for abstraction of H atoms by Cl atoms are much larger than those for abstraction by OH radicals from the same alkanes, despite the greater exothermicities of the latter reactions. From the data given in Table 1, it is apparent that the increase in the rate constants for reactions of higher alkanes is associated, at least in part, with a lowering of the activation energy and presumably of the barrier to reaction on the minimum-energy path, although the actual magnitude of these barriers cannot easily be inferred from the activation energies given in Table 1 because there is evidence for the curvature of Arrhenius plots for these reactions. It is usually assumed that this lowering of the barrier to reaction is connected with the lowering of the C–H bond energy from  $439 \text{ kJ mol}^{-1}$  for  $\text{CH}_3\text{--H}$  to  $420.5 \text{ kJ mol}^{-1}$  for  $\text{C}_2\text{H}_5\text{--H}$ , to  $401 \text{ kJ mol}^{-1}$  for  $(\text{CH}_3)_2\text{CH--H}$ , and to  $399 \text{ kJ mol}^{-1}$  for  $(\text{CH}_3)_3\text{C--H}$ .

Donahue and co-workers<sup>9,10</sup> have argued persuasively that the correlation between activation energies and C–H bond energies is coincidental. They propose that the height of the barrier to reaction is determined by the coupling between ground and ionic excited-state surfaces; the smaller the separation between these surfaces, the stronger the coupling and the smaller the barrier to reaction. In this model, the lowering of the activation energy for the reaction of a given radical (e.g., OH or Cl) with the series of alkanes is associated with the decrease in ionization energies of the alkanes, which for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  have the values 12.51, 11.52, and  $10.95 \text{ eV}$ .<sup>4</sup> For the reactions of OH radicals, Donahue et al.'s model leads to barrier heights close to the experimentally determined activation energies. More to the point and within the context of the present article, the model leads to the reaction of Cl with a given alkane having a smaller barrier than the reaction of OH with the same alkane. For example, for  $\text{Cl} + \text{CH}_4$ ,  $E_a/R$  is estimated to be 1350 K, whereas for  $\text{OH} + \text{CH}_4$ ,  $E_a/R$  is estimated to be 1800 K.<sup>9a</sup>

Ideas of this kind, together with the large amount of accurate kinetic data available for these reactions, have led to a number of attempts<sup>16,17</sup> to construct structure–activity relationships for these and other similar reactions to make it possible to predict the rate constants for reactions for which direct measurements may not be possible. In the present article, we compare the rate

constants and activation energies for reactions of OH and Cl with the same co-reagent. When the OH radical reacts faster, it provides some evidence that there may be a mechanism involving hydrogen bonds that provides a lower-energy path to reaction than direct H-atom abstraction. In considering the kinetic data for reactions involving co-reagents other than alkanes, it is important to bear in mind the caution expressed by Donahue et al. that one should consider ionic surfaces resulting from the promotion of electrons involved in the bond-breaking/bond-making process.

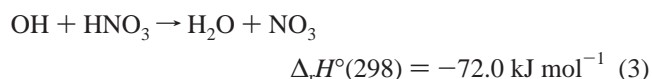
Gierczak et al.<sup>18</sup> have measured rate constants for the reactions of OH with partially and fully deuterated  $\text{CH}_4$  as well as for the reaction of OD with  $\text{CH}_4$  between ca. 200 and 415 K using pulsed-laser photolysis to generate OH/OD and laser-induced fluorescence of OH/OD to observe kinetic decays. Their results for  $\text{OH} + \text{CD}_4$  and  $\text{OD} + \text{CH}_4$  are given in Table 1. Comparison of the data for  $\text{OH} + \text{CH}_4$  and  $\text{OH} + \text{CD}_4$  shows a primary isotope effect:  $k(\text{OH} + \text{CH}_4)/k(\text{OH} + \text{CD}_4) = 7.2$  at 298 K, whereas the data for  $\text{OH} + \text{CH}_4$  and  $\text{OD} + \text{CH}_4$  yields a secondary isotope effect of 0.93 (or close to unity).

As mentioned earlier, according to the ideas of transition-state theory, the principal cause of fairly large primary kinetic isotope effects in direct reactions is the lowering of  $\Delta E_0^\ddagger$ , the difference in the zero-point energies in the transition state and in the separated reagents when a D atom rather than an H atom is transferred. Substitution of D for H elsewhere in the reaction system, for example using OD rather than OH as the radical, affects  $\Delta E_0^\ddagger$  only slightly and has a much smaller effect on the rate coefficient. These general ideas have been elaborated on by a number of groups including Truhlar and co-workers<sup>19</sup> who used variational transition-state theory with multidimensional tunneling and an ab initio potential energy surface to calculate rate constants at different temperatures. In general, the calculated rate constants matched the experimental results of both Gierczak et al. and Dunlop and Tully<sup>20</sup> rather well.

In summary, the evidence appears to be overwhelming that the reactions of OH with the simpler alkanes proceed directly, without influence from any weak potential energy wells in the entrance valley of the potential energy surface. In the context of the present article, these reactions serve as a useful benchmark against which to compare the kinetic data for other reactions to determine if evidence exists for the influence of hydrogen bonding, either through the formation of transitory complexes or by affecting the dynamics of the reactive collisions.

## 2.b. Reaction between OH Radicals and $\text{HNO}_3$

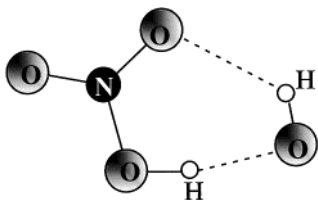
Nitric acid is one of the most abundant active nitrogen species in the atmosphere, and it is an important reservoir for  $\text{NO}_x$  radicals that play crucial roles in the chemistry of both the troposphere and the stratosphere.<sup>1</sup> The reaction of  $\text{HNO}_3$  with OH radicals,



is a major pathway for regenerating  $\text{NO}_x$  from this reservoir. This reaction is also a major sink for  $\text{HO}_x$  in the lower stratosphere. Its atmospheric importance as well as its interesting kinetic features has led to this reaction being the subject of a large number of laboratory investigations<sup>2,3</sup> as well as theoretical studies.<sup>21,22</sup>

Although the earliest direct kinetic measurements<sup>23</sup> failed to recognize the unusual temperature and pressure dependences of this reaction, they did demonstrate that its rate constant was



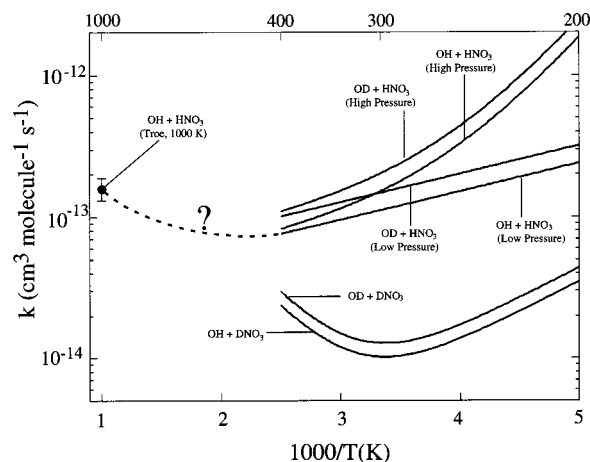


**Figure 1.** Structure of the weakly bound intermediate in the reaction of OH with HNO<sub>3</sub>.

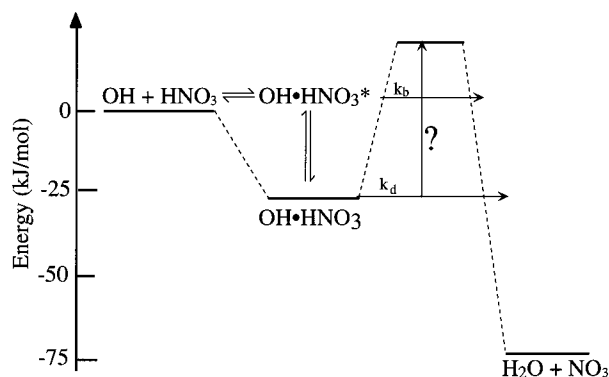
surprisingly small given that it showed little or no variation with temperature at and around 298 K. Subsequent studies showed that the rate coefficient for this reaction had a negative temperature dependence and possibly a slight pressure dependence.<sup>2,3</sup> This discovery significantly altered the perceived role of the OH + HNO<sub>3</sub> reaction in stratospheric ozone depletion due to CFCs and nitrogen oxides. Besides confirming the unusual effects of temperature and pressure on the rate of this reaction (and those involving the isotopomers of OH and HNO<sub>3</sub>), more recent studies<sup>24,25</sup> have also shown unequivocally that the yield of H<sub>2</sub>O + NO<sub>3</sub> from this reaction is unity within experimental error, that the system exhibits kinetic isotope effects that are not those expected for a direct H-atom abstraction reaction, and that the mechanism does not lead to significant exchange either of H/D isotopes in the reactions of OH with DNO<sub>3</sub> and OD with HNO<sub>3</sub> or of <sup>18</sup>O/<sup>16</sup>O in the reaction of <sup>18</sup>OH radicals with normal HNO<sub>3</sub>. Moreover, at 298 K, the analogous reaction of Cl atoms with HNO<sub>3</sub> is more than two orders of magnitude slower than the reaction of OH with HNO<sub>3</sub>:  $k_{298}(\text{Cl} + \text{HNO}_3) < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>2,3</sup> compared with  $k_{298}(\text{OH} + \text{HNO}_3) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in the limit of zero total pressure.<sup>2,3</sup> This finding is in sharp contrast to those for the direct reactions of OH and Cl with alkanes, where Cl atoms react consistently faster than OH radicals.

The observed behavior of the OH + HNO<sub>3</sub> reaction with respect to temperature and pressure has led several groups to propose that the reaction proceeds via a mechanism involving an addition complex. Marinelli and Johnston<sup>26</sup> were the first to propose that this complex might involve hydrogen bonding; Lamb et al.<sup>27</sup> preferred a complex in which a weak bond forms between the O atom of the hydroxyl radical and the N atom in the nitric acid molecule. On the bases of their results on isotope exchange, of quite detailed modeling of the kinetics, and of the ab initio calculations of Aloisio and Francisco,<sup>21</sup> Brown et al.<sup>25</sup> have argued for the importance of a complex of the form shown in Figure 1. It is bound by two hydrogen bonds in a six-membered cyclic structure and has a dissociation energy of ca. 25 kJ mol<sup>-1</sup> relative to the energy of the separated reagents. Lin and co-workers<sup>22</sup> have come to the same conclusion on the basis of detailed calculations of the structures of the adduct and microcanonical variational RRKM calculations that fit the data of Brown et al.<sup>24,25</sup> to a falloff curve.

Figure 2 shows how the rate constants of Brown et al.<sup>24,25</sup> depend on temperature for the different isotopic variations of reaction 3 in the limits of low and high pressure (close to 1 atm). It is especially noteworthy that the rate constants for OH, OD + HNO<sub>3</sub> are much greater than those for OH, OD + DNO<sub>3</sub> and that OD reacts faster than OH with both HNO<sub>3</sub> and DNO<sub>3</sub>. In addition, the rate constants for all the reactions show a negative dependence on temperature below room temperature, that is, they increase as the temperature falls. All these results, together with the observed dependences on total pressure, are well matched by calculations based on the adduct whose structure is shown in Figure 1 and the mechanism that is shown schematically in Figure 3.



**Figure 2.** Pictorial representation of the rate coefficients for the reactions of OH and OD with HNO<sub>3</sub> and DNO<sub>3</sub> as a function of temperature.



**Figure 3.** Schematic diagram of the mechanism for and energetics in the reaction of OH with HNO<sub>3</sub>.

A crucial part of the hypothesis is that the hydrogen-bonded adduct is separated from the H<sub>2</sub>O + NO<sub>3</sub> products by a significant energy barrier so that, in the absence of stabilizing collisions, the majority of the energized adducts, OH·HNO<sub>3</sub><sup>\*</sup>, that form in collisions between OH and HNO<sub>3</sub> redissociate to OH + HNO<sub>3</sub>. Another result of the barrier separating OH·HNO<sub>3</sub> from H<sub>2</sub>O + NO<sub>3</sub> is that the reaction to H<sub>2</sub>O + NO<sub>3</sub> proceeds via the H atom from HNO<sub>3</sub> tunneling through the barrier that separates the OH·HNO<sub>3</sub> potential energy well from the product asymptote. The reason that there is a large kinetic isotope effect between the rate constants for OH, OD + HNO<sub>3</sub> and OH, OD + DNO<sub>3</sub> has little to do with the difference in zero-point energies at the transition states and reagent asymptotes, as in the case of H-atom abstraction reactions such as those of OH with alkanes. Rather, it is because the H atom transferred in the OH, OD + HNO<sub>3</sub> reactions can tunnel faster than the D atom transferred in the OH, OD + DNO<sub>3</sub> reactions.

The reaction of OH with CH<sub>3</sub>ONO<sub>2</sub>, unlike the reaction of OH with HNO<sub>3</sub>, exhibits a positive temperature dependence consistent with direct H-atom abstraction as in the case of alkanes.<sup>2,3</sup> Even though CH<sub>3</sub>ONO<sub>2</sub> is very similar to HNO<sub>3</sub>, its reaction with OH is not facilitated by the formation of a hydrogen-bonded complex. It is noteworthy that the rate coefficient for the reaction of CH<sub>3</sub>ONO<sub>2</sub> with Cl is an order of magnitude larger than that with OH at 298 K.<sup>3</sup> These observations are consistent with our contention that the adduct formation increases the rate coefficient for the OH reaction relative to that

for the Cl atom and leads to negligible or negative temperature dependence.

In summary, the reaction between OH and HNO<sub>3</sub> appears to be clearly established as the prototype of reactions of OH that can proceed via a hydrogen-bonded adduct that lives sufficiently long with respect to unimolecular redissociation to be treated, at least approximately, as an intermediate by the usual steady-state approximations. The model calculations carried out by Brown et al.<sup>25</sup> fit the current experimental data quite well, and the main features of their mechanistic explanation are supported by the more extensive theoretical calculations of Xia and Lin.<sup>22</sup> Their quantum chemical calculations predict that two OH·HNO<sub>3</sub> complexes are involved in the dynamics of this reaction: a six-membered ring structure with a binding energy of 34 kJ mol<sup>-1</sup> that is separated from H<sub>2</sub>O + NO<sub>3</sub> by a barrier of 48.5 kJ mol<sup>-1</sup> and a five-membered structure with a binding energy of 22 kJ mol<sup>-1</sup> and a barrier to decomposition to H<sub>2</sub>O + NO<sub>3</sub> of 27.5 kJ mol<sup>-1</sup>. Their rate constant calculations suggest that reaction occurs via both these routes and that quantum mechanical tunneling through the barriers separating the potential wells associated with the complexes from the H<sub>2</sub>O + NO<sub>3</sub> products is an important influence on the kinetic isotope effects.

On the experimental side, new measurements have been made<sup>28</sup> of the rates of relaxation of OH(*v* = 1) and OD(*v* = 1) by HNO<sub>3</sub> and DNO<sub>3</sub> and their temperature dependences. The rate constant for relaxation of OH(*v* = 1) by HNO<sub>3</sub> at room temperature is  $2.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,<sup>29</sup> more than two orders of magnitude greater than that for reaction of OH with HNO<sub>3</sub> at the same temperature. This unusually rapid rate of relaxation for a high-frequency vibration may have two causes: it may reflect the possibility of near-resonant vibration–vibration (V–V) energy exchange between OH and the O–H stretching vibration in HNO<sub>3</sub>, or it may reflect the ease of energy transfer via the bound complex that plays a role in the OH + HNO<sub>3</sub> reaction. The latter of these two mechanisms should operate, with comparable efficiencies, for all four isotopic variants. On the other hand, V–V exchange between OH(*v* = 1) and DNO<sub>3</sub> and OD(*v* = 1) and HNO<sub>3</sub> should be appreciably slower than that between OH(*v* = 1) and HNO<sub>3</sub> and OD(*v* = 1) and DNO<sub>3</sub> because of the lack of close resonance between the vibrational frequencies in the first two cases (and in OD(*v* = 1) + HNO<sub>3</sub> because V–V exchange is strongly endothermic). Preliminary results obtained in these systems support the notion that relaxation is rapid because of the formation of transient, moderately bound complexes.<sup>28</sup>

## 2.c. Reactions of OH with Carboxylic Acids, Aldehydes, and Ketones<sup>62</sup>

Carboxylic acids, aldehydes, and ketones all contain carbonyl groups that are known to form strong hydrogen bonds with H-atom donors. For example, complexes of HF with H<sub>2</sub>CO have been thoroughly studied,<sup>5,30</sup> and the spectroscopic evidence points to the formation of a strong hydrogen bond. In addition, dimers of carboxylic acids are one of the best-known examples of species held together by hydrogen bonds. In each dimer, there are two hydrogen bonds, each between the acidic H atom of one monomer and the O atom of the C=O group on the other, forming an eight-membered ring structure and yielding an overall dissociation energy of approximately 60 kJ mol<sup>-1</sup>.<sup>31</sup> One has to take careful account of this dimerization in the interpretation of any kinetic measurements on reactions of a carboxylic acid where first-order conditions apply with the acid in excess over the radical, for example, OH or Cl atoms.

**TABLE 2: Comparison of Rate Constants (*k*<sub>d</sub>/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and Activation Energy (*E*<sub>a</sub>(R)/K) at 298 K for the Reactions of OH, OD, and Cl with Carboxylic Acids**

reagent	OH	OD	Cl
HCOOH	$4.5 \times 10^{-13}$ ( $-102 \pm 194$ ) <sup>32</sup> $4.7 \times 10^{-13}$ ( $-77 \pm 75$ ) <sup>33</sup>		$1.8 \times 10^{-13}$ <sup>34</sup>
DCOOH	$4.0 \times 10^{-13}$ <sup>32</sup> $4.0 \times 10^{-13}$ <sup>33</sup>		
DCOOD		$6.1 \times 10^{-14}$ ( $594 \pm 134$ ) <sup>32</sup>	
CH <sub>3</sub> COOH	$8.7 \times 10^{-13}$ <sup>35</sup>		$2.8 \times 10^{-14}$ <sup>35</sup>
CD <sub>3</sub> COOH	$8.1 \times 10^{-13}$ <sup>35</sup>		
CD <sub>3</sub> COOD	$2.35 \times 10^{-13}$ <sup>35</sup>		
CH <sub>3</sub> CH <sub>2</sub> COOH	$1.1 \times 10^{-12}$ <sup>35</sup>		

There have been several studies of the reactions of OH with both HCOOH and CH<sub>3</sub>COOH with the objective of determining rate constants as well as the mechanism of reaction. For OH + HCOOH, both Singleton and co-workers<sup>32</sup> and Wine et al.<sup>33</sup> have measured rate constants over a range of temperatures and have conducted experiments designed to determine which H atom is abstracted from the HCOOH molecule:



or



The results of their kinetic measurements are shown in Table 2. Where the rate constants can be compared, they are in good agreement. As with reaction 3, the rate constant for reaction 4 is found to be essentially independent of temperature but to have quite a small value at 298 K. However, in this case, the rate constant shows no dependence on the total pressure.

Circumstantial evidence indicates that OH predominantly abstracts the acidic H atom rather than the other hydrogen, despite the higher energy of the O–H bond compared to that of the C–H bond. First, there are the relative values of the rate constants shown in Table 2. Substitution of D for H in the acidic position brings about a substantial lowering of the rate constant for reaction, whereas substitution in the other position brings about only a small change. Second, Singleton and co-workers<sup>32</sup> extracted rate constants for the reactions of OH and OD with dimers of HCOOH and DCOOH by nonlinear fitting of their measured pseudo-first-order rate constants. Although the errors in the rate constants derived for reactions of the dimers were large, it was quite clear that the dimers in which the H atoms participating in the hydrogen bonds are shielded but the other H atoms are exposed and essentially unaffected by dimer formation reacted appreciably slower than the monomers. Finally, the observation of near-unity yields of H atoms is also consistent with abstraction of the acidic H atom followed by rapid dissociation of the HCOO product of reaction 3b.

Wine et al.<sup>33</sup> concluded that the absence of any temperature dependence of the rate constants suggests that reaction proceeds via a complex rather than a direct mechanism and hypothesized that OH might add to the carbonyl double bond. Singleton and co-workers<sup>32</sup> subsequently invoked the participation of a hydrogen-bonded adduct. Although they did perform some model calculations in which the adduct could redissociate to OH + HCOOH or rearrange and dissociate to H<sub>2</sub>O + HCOO, they did not include the possibility of collisional stabilization of the initially formed adduct, nor did they discuss whether any barrier separated the adduct from the product asymptote.

Our own view is that this system may strongly resemble the OH + HNO<sub>3</sub> system that we have already discussed. OH could add to formic acid (and, indeed, other carboxylic acids) by forming a six-membered ring, with minimal ring strain, held together by two hydrogen bonds. Formation of the products would then require intramolecular transfer of the acidic H atom to the OH. This process is likely to have a barrier associated with it, and the large isotope effect is likely, as with OH + HNO<sub>3</sub>, to be attributable to the different rates at which H and D atoms can tunnel through this barrier. Studies of these reactions over a wide range of temperature, especially below 200 K, should reveal the type of behavior observed for the OH + HNO<sub>3</sub> reaction if complex formation is important, although care will have to be exercised to exclude effects due to increased formation of formic acid dimers.

Further indirect evidence for the unimportance of abstraction of the formyl H atom in the reaction of OH with HCOOH comes from the fact that the rate constant for Cl + HCOOH, a reaction that abstracts the formyl H atom and yields HCl + COOH, is  $1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>34</sup> This value is less than half that for OH + HCOOH, which yields HCOO + H<sub>2</sub>O, whereas comparisons of the rate constants for H abstraction from alkanes (see section 2.a.) would suggest that abstraction by Cl should be significantly faster than abstraction by OH.

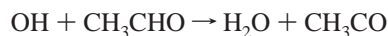
Singleton et al.<sup>35</sup> have also investigated the kinetics and mechanisms of the reactions of OH radicals with CH<sub>3</sub>COOH, CD<sub>3</sub>COOH, CD<sub>3</sub>COOD, and CH<sub>3</sub>CH<sub>2</sub>COOH at temperatures between 297 and 446 K. The rate constants that they determined at 298 K are listed in Table 2. For OH + CH<sub>3</sub>CH<sub>2</sub>COOH, the rate constants are independent of temperature. The Arrhenius plots for all three of the reactions involving isotopomers of acetic acid are markedly curved, the rate constants decreasing as the temperature is raised until they flatten off at about 400 K. Consequently, activation energies are not cited. At higher temperatures, the rate constants for these reaction may start to show a positive temperature dependence. Singleton et al.'s interpretation of their results for OH + CH<sub>3</sub>COOH and its isotopomers mirrors that given for the reactions of OH with HCOOH and its isotopomers.

Again, we would propose that the adduct formed from OH + acid is likely to involve two hydrogen bonds and that dissociation of this species to products probably involves tunneling through a potential energy barrier, thus contributing to the relatively large isotope effect that is seen when the acidic H atom is replaced by D.<sup>32,33</sup> The rate constants for the reaction of OH with propionic acid are independent of temperature and are larger than those found for OH + CH<sub>3</sub>COOH, which is interpreted as being due to the increasing rate of H-atom abstraction from the alkyl group when secondary C–H bonds are present, as is seen (see section 2.a.) for the reactions of OH with alkanes. Finally, we note that Cl atoms react appreciably more slowly with CH<sub>3</sub>COOH,  $k(298 \text{ K}) = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>36</sup> than do OH radicals and that they abstract methyl, rather than acidic, H atoms. This is again consistent with the notion that OH radicals react with the simpler carboxylic acids, HCOOH and CH<sub>3</sub>COOH, via a hydrogen-bonded intermediate involving the –COOH group and subsequent abstraction of the acidic H atom.

There is an increasing amount of theoretical evidence<sup>37,38</sup> that OH radicals can form strong hydrogen bonds with species containing a carbonyl group. Here we review the evidence that such weakly bound species either act as transitory intermediates in the reactions of OH with CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> or that

forces created by hydrogen bonds influence the dynamics of these reactive collisions.

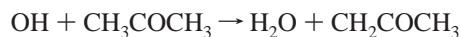
Interpretation of the kinetic data for reactions of OH radicals with aldehydes is confused by two factors: the relative scarcity of data, for example, on isotope effects, despite the importance of these reactions in the breakdown of hydrocarbons in the atmosphere and the weakness of the aldehydic C–H bond. Thus, in acetaldehyde, the enthalpy of the aldehydic bond  $D(\text{CH}_3\text{C}(\text{O})\text{--H}) = 374 \text{ kJ mol}^{-1}$ , which compares with the values of  $D((\text{CH}_3)_2\text{CH--H}) = 401 \text{ kJ mol}^{-1}$  and  $D((\text{CH}_3)_3\text{C--H}) = 399 \text{ kJ mol}^{-1}$  that were given earlier. In light of these figures, it is not surprising that the rate constant for the OH + CH<sub>3</sub>CHO reaction



$$\Delta_r H^\circ = -139.6 \text{ kJ mol}^{-1} \quad (5)$$

is  $k_5(298 \text{ K}) = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and shows a slightly negative temperature dependence.<sup>2,3</sup> In other words, there seems to be little need to invoke a strong role for the hydrogen-bonded configuration that almost certainly exists between OH and CH<sub>3</sub>CHO. Such OH–CH<sub>3</sub>CHO adducts have been proposed and their role discussed previously.<sup>39,40</sup> Even if reactive collisions proceed via this potential energy minimum, it seems likely that there is no barrier to reaction between this minimum and the products CH<sub>3</sub>CO + H<sub>2</sub>O. This interpretation of the dynamics of OH + CH<sub>3</sub>CHO reactive collisions is supported by the fact that the reaction of Cl atoms with CH<sub>3</sub>CHO,  $k(298 \text{ K}) = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is even faster than that of OH radicals with CH<sub>3</sub>CHO and shows no temperature dependence.<sup>2,3</sup>

The situation with respect to the reaction between OH radicals and acetone is especially intriguing. In 1997, when the IUPAC and NASA evaluations were published,<sup>2,3</sup> the rate constant at 298 K was fairly well-established,  $k_6(298 \text{ K}) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , but there had been rather few investigations of the temperature dependence of the rate coefficient and none of isotope effects. Moreover, the reaction was assumed to proceed entirely by H-atom abstraction:

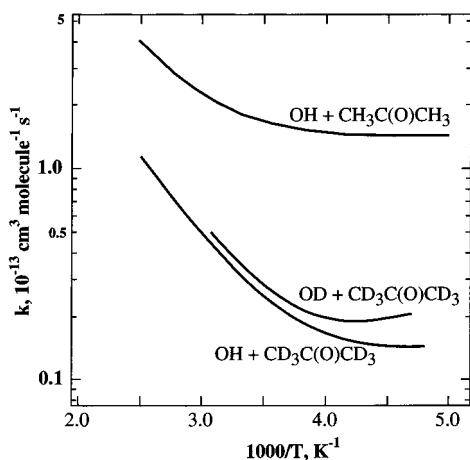


$$\Delta_r H^\circ = -87.8 \text{ kJ mol}^{-1} \quad (6a)$$

Since then, a number of experimental<sup>38,41–45</sup> and theoretical<sup>37,38</sup> studies have been carried out on this reaction. Although the rate constant for the overall reaction at 298 K has remained essentially unchanged, there have been suggestions that other data for this reaction should be revised. Measurements by Le Calve et al.,<sup>44</sup> Wollenhaupt et al.,<sup>41</sup> and Gierczak et al.<sup>43</sup> have demonstrated that the rate exhibits an unusual temperature dependence, with the overall rate constant increasing above room temperature but becoming essentially constant at and below about 250 K.

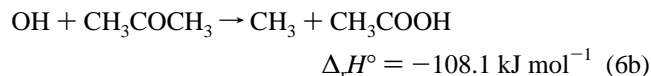
Gierczak et al.<sup>43</sup> also thoroughly explored the kinetic isotope effects in this reaction, demonstrating a relatively large primary effect,  $k(\text{OH} + \text{CH}_3\text{COCH}_3)/k(\text{OH} + \text{CD}_3\text{COCD}_3) = 5.9 \pm 0.9$  at 298 K, and a very small secondary isotope effect,  $k(\text{OH} + \text{CH}_3\text{COCH}_3)/k(\text{OD} + \text{CH}_3\text{COCH}_3) = 0.84 \pm 0.09$  at 298 K. Figure 4 shows an Arrhenius plot of their data<sup>43</sup> for OH + CH<sub>3</sub>COCH<sub>3</sub>, OH + CD<sub>3</sub>COCD<sub>3</sub>, and OD + CD<sub>3</sub>COCD<sub>3</sub>. In addition, Gierczak et al.<sup>43</sup> demonstrated that the rate of reaction between OH radicals and CH<sub>3</sub>COCH<sub>3</sub> shows no dependence on the total pressure, even in 500 Torr of added SF<sub>6</sub> at 250 K.





**Figure 4.** Schematic representation of the rate coefficients for the reactions of OH and OD with  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  and  $\text{CD}_3\text{C}(\text{O})\text{CD}_3$  that were measured by Gierczak et al.<sup>43</sup>

Although the overall rate constants for  $\text{OH} + \text{CH}_3\text{COCH}_3$  measured by Wollenhaupt and Crowley<sup>42</sup> and by Vasvári et al.<sup>38</sup> and their temperature dependence agree very well with those determined by Gierczak et al.,<sup>43</sup> the former two groups report evidence that  $\text{CH}_3$  radicals are formed as a direct product of this reaction, namely, by the channel



Vasvári et al.<sup>38</sup> measured the yield of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2$  to be roughly 50% at 298 K. Furthermore, Wollenhaupt and Crowley<sup>42</sup> report that the yield of  $\text{CH}_3$  falls from 0.5 at room temperature to 0.3 at 230 K. Vasvári et al.<sup>38</sup> suggest that the two channels, 6a and 6b, proceed by a common hydrogen-bonded intermediate, and their calculations reproduce the experimental result of equal branching to both channels at room temperature. Wollenhaupt and Crowley measured the yield of  $\text{CH}_3$  to decrease with decreasing temperature, an observation that is hard to reconcile with the proposed mechanism. They acknowledge, however, that uncertainties remain with respect to how the branching ratios depend on temperature, and it is also not clear whether these results are consistent with the large primary isotope effect observed by Gierczak et al.<sup>43</sup> that increases with decreasing temperature. The large kinetic isotope effect is inconsistent with the breaking of a C–C bond being the rate-limiting step in this reaction; it would argue for the involvement of a H-atom transfer. In addition, very recent experiments contradict the conclusions of Wollenhaupt and Crowley<sup>42</sup> and Vasvári et al.<sup>38</sup> regarding the importance of reaction 6b. Gierczak et al.<sup>43</sup> find that less than 0.1% of the overall reactions of OH radicals with  $\text{CH}_3\text{COCH}_3$  produce  $\text{CH}_3\text{COOH}$ . Furthermore, two other recent studies<sup>45</sup> report upper limits of 5–10% for the formation of  $\text{CH}_3\text{COOH}$  as a product of the reaction between OH and  $\text{CH}_3\text{COCH}_3$ .

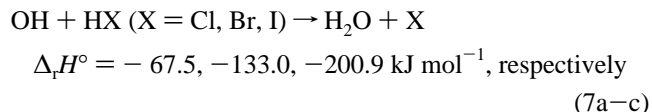
Aloisio and Francisco<sup>37</sup> and Vasvári et al.<sup>38</sup> have carried out ab initio calculations to explore the energies and structures of any adducts that might be formed from OH radicals and  $\text{CH}_3\text{COCH}_3$ . Using density functional theory, Aloisio and Francisco found one minimum corresponding to a hydrogen-bonded structure in which a strong hydrogen bond was formed between the H atom of the OH and the O atom of  $\text{CH}_3\text{COCH}_3$  and a weaker hydrogen bond was formed between the O atom of the OH and one of the methyl H atoms in  $\text{CH}_3\text{COCH}_3$ . Recognizing the importance of reaction 6, Vasvári et al. explored the potential

energy surface more widely. They found two hydrogen-bonded structures, one (MC1) like that determined by Aloisio and Francisco and a second (MC2) in which, as well as the primary hydrogen bond, there is weak attraction between the carbonyl C atom and the O atoms of the hydroxyl. They went on to calculate transition states for the transformation of structure MC1 to  $\text{H}_2\text{O} + \text{CH}_2\text{COCH}_3$  and of MC2 to  $\text{CH}_3 + \text{CH}_3\text{COOH}$ .

To summarize, we conclude that weakly bound adducts in which one or two hydrogen bonds play a key role appear to play an important part in the reaction between OH radicals and acetone. The large primary kinetic isotope effect may be the result both of zero-point effects and of different rates of H-atom and D-atom tunneling through barriers separating the structures of these complexes from the products of reactions 5a and 5b.

## 2.d. Reactions of OH with Hydrogen Halides

The halogen atoms Cl, Br, and I all play important roles in the atmosphere. Chlorine and bromine are present in the stratosphere and are known to destroy ozone. Iodine is also expected to be very efficient in destroying ozone, if it gets there. Iodine is known to play an important role in the troposphere. The hydrogen halides HCl, HBr, and HI are all major sinks for active forms of the halogens in the atmosphere. Their reactions with OH radicals are important, as they convert these reservoir compounds to active forms that can participate in catalytic ozone destruction. Consequently, the three reactions



have been studied quite extensively.

The kinetic behavior of the  $\text{OH} + \text{HCl}$  reaction around room temperature has been well established,  $k_{7a}(298 \text{ K}) = 8.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>2,3</sup> However, there remain questions about the temperature dependence of the rate constant at low temperatures. Sharkey and Smith<sup>46</sup> have measured rate constants for reaction 7a at temperatures down to 138 K, finding very little change with temperature below about 200 K. The experimental results of Ravishankara and co-workers<sup>47</sup> down to 200 K agree well with those of Sharkey and Smith, although they fit their data to transition-state calculations that deviate significantly and increasingly from Sharkey and Smith's results at the lower temperatures.

More recently, Battin-Leclerc et al.<sup>48</sup> have investigated the kinetics of all four H/D isotopic variants of reaction 7a (i.e.,  $\text{OH} + \text{HCl}$ ,  $\text{OH} + \text{DCl}$ ,  $\text{OD} + \text{HCl}$ , and  $\text{OD} + \text{DCl}$ ) at temperatures between 200 and 400 K. The results are what one would expect in terms of a conventional analysis of the kinetic isotope effects. That is, the rates are lowered appreciably when DCl is substituted for HCl but are altered only slightly when OD replaces OH.

Steckler et al.<sup>49</sup> have performed variational transition-state theory calculations on the  $\text{OH} + \text{HCl}$  reaction using scaled ab initio calculations to define the minimum-energy path and the vibrational frequencies orthogonal to it. They obtain remarkably good agreement with experiment. In particular, the rate constants that they calculate show appreciable curvature on an Arrhenius plot, exhibiting the lack of dependence on temperature below 200 K that is a feature of Sharkey and Smith's experimental results.

Of course, our purpose here is to explore if there is any evidence for the influence of hydrogen bonding on the reaction dynamics. Spectroscopic experiments on  $\text{HF-HCl}$  complexes<sup>50</sup>

reveal that the most strongly bound complex has a dissociation energy of  $D_0 = 7.7 \text{ kJ mol}^{-1}$  and a structure that, if repeated for HO–HCl, would serve as a suitable prereaction intermediate. Forces of similar strength in the case of HO–HCl would create a minimum along the reaction path of comparable magnitude to the barrier height. Furthermore, the rate constant might be expected to depend on the rotational states of the reagents, higher rotational states being less affected by long-range forces directing the reagents into favorable orientations for reaction.

In keeping with its greater exothermicity, the reaction between OH and HBr occurs faster than that between OH + HCl,  $k_{7b}(298 \text{ K}) = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>2,3</sup> and around 298 K, its rate constant is independent of temperature.<sup>51</sup> However, reaction 7b is the one reaction of OH radicals in which a H atom is abstracted that has been studied at very low temperatures (down to 23 K).<sup>52,53</sup> As the temperature is lowered below about 200 K, the rate constant starts to rise steeply, reaching its highest value,  $k_{7b}(298 \text{ K}) = 1.07 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , at 23 K. This observation shows that this reaction proceeds over a potential energy surface with no barrier between reagents and products.

Clary and co-workers<sup>54,7b</sup> have calculated the rate constants for OH + HBr and for OH + HCl by a variety of theoretical methods. In relatively simple adiabatic capture calculations, like those employed successfully for reactions between ions and polar molecules, they calculated rate constants for OH + HBr while assuming that the long-range potential responsible for capture arose from the dipoles on the two reagents. Although the absolute values of the rate constants were greater than those found experimentally,<sup>51</sup> their negative temperature dependence above 20 K mirrored that observed. At least in part, this increase as the temperature is lowered results from the increase in rotationally selective rate constants as the rotational quantum number decreases, and it becomes more likely that the dipole–dipole potential will orient the reagents favorably for reaction.

Clary et al.<sup>7b</sup> have also undertaken quantum scattering calculations on OH + HBr and OH + HCl within the rotating bond approximation. Once again, the rate constants are found to depend strongly on the rotational state of the OH radical, but the explanation for this dependence is rather different. Now for OH it is attributed to the strong correlation between the (*j*, *K*) states and the ground and excited bending states of H<sub>2</sub>O. Consequently, the adiabatic barriers do depend on (*j*, *K*). This theory takes no account of the long-range electrostatic potential between the two dipolar reagents. The results reproduce not only the negative dependence of the rate constants for OH + HBr but also the very slight dependence of the rate constants for OH + HCl on temperature below 298 K.

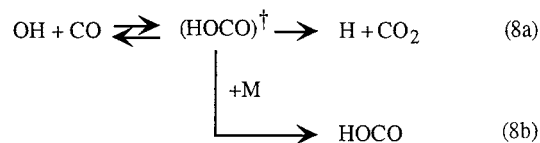
The kinetics of the OH + HI reaction continue the trend of increasing rate constants as the HX bond energy decreases (or the exothermicity of reaction 7 increases). The rate constant at room temperature is  $k_{7c}(298 \text{ K}) = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and between 246 and 353 K, the rate constant increases with decreasing temperature according to a  $T^{-1.5}$  dependence.<sup>55</sup>

At present, it seems impossible to arrive at any definite conclusion about how the dynamics of collisions between OH + HCl and OH + HBr, and hence their reaction kinetics, are affected by the relatively strong dipole–dipole (or hydrogen-bonding) forces that act as OH approaches the hydrogen halides.

## 2.e. Reaction of OH with CO

The reaction between OH radicals and CO is almost entirely responsible for converting CO to CO<sub>2</sub> in the Earth's atmosphere and in combustion systems.<sup>1</sup> In addition, it exhibits very

interesting dynamics in that it proceeds by way of an energized HOCO complex that can redissociate to OH + CO, dissociate to products H + CO<sub>2</sub>, or be stabilized in collisions to HOCO radicals. Both of these features have led to its kinetics and



dynamics being extensively studied both experimentally<sup>56–58</sup> and theoretically<sup>59,60</sup> over the past three decades.

The rate constant for reaction 8a, that is, for reaction at pressures too low for significant collisional stabilization of (HOCO)<sup>‡</sup>, is rather small,  $k_8(298 \text{ K}) = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and exhibits very little dependence on temperature from 500–80 K.<sup>2,3</sup> There is a significant isotope effect. Thus, at 298 K,  $k_8(\text{OH} + \text{CO})/k_8(\text{OD} + \text{CO}) = 2.8$ .<sup>56</sup> In the limit of high pressure,  $k_8(298 \text{ K}) = 9.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>58</sup> and both this value and the rate constant for relaxation of OH(*v* = 1) by CO<sup>56</sup> are assumed to be that for the initial formation of the (HOCO)<sup>‡</sup> complex.

The mechanism that is accepted for reaction 8 is that it proceeds over a low barrier (TS1) to form the chemically bound HOCO species, which corresponds to a deep potential energy well along the reaction path. Between this well and the H + CO<sub>2</sub> product asymptote is a barrier (TS2) whose energy is close to that of the OH + CO reagent asymptote. These are the features of the potential energy surface that are mainly responsible for the unusual temperature and pressure dependences that are found for the rate constant for this reaction<sup>56–58</sup> and that are outlined in the previous paragraph.

However, using transition-state theory, Frost et al.<sup>57</sup> and others have only been partially successful in modeling all of the kinetic features of the reaction. For example, they were unable simultaneously to explain the values of the observed rate constants at low temperature (down to 80 K) and the high-pressure limit<sup>58</sup> of the rate constant. In an attempt to model all the kinetic behavior of the OH + CO reaction, they explored whether a hydrogen-bonded complex between OH and CO might act as a precursor state for the formation of energized HOCO complexes via TS1. By comparison with the measured bonding energies of the XH–CO complexes (X = F, Cl, and Br), they estimated that the OH–CO adduct would have a binding energy of  $(D_0/hc) \approx 450 \text{ cm}^{-1}$ . This value is quite similar to that estimated in ab initio calculations by Lester et al.<sup>60</sup>  $((D_0/hc) \approx 405 \text{ cm}^{-1})$  and by Kudla et al.<sup>61</sup>  $((D_0/hc) \approx 600 \text{ cm}^{-1})$ . These energies are higher than both the thermal energy in low-temperature experiments and the inferred adiabatic barrier at TS1. However, in contrast to the case of OH radicals reacting with hydrogen halides, in this case the structure of the hydrogen-bonded complex is not that required for passage through TS1. In simple terms, it is OH–CO rather than HO–CO, and Frost et al.'s efforts<sup>57</sup> to model the role of the hydrogen-bonded complex on the kinetics of reaction 8 were not successful. However, the calculations reported by Lester et al.<sup>60</sup> do suggest a smooth reaction path from the minimum associated with OH–CO over a shallow barrier to *trans*-HOCO.

More recently, Lester and co-workers<sup>60</sup> have created the OH–CO adduct in supersonic expansions and studied the structure and binding energy of this hydrogen-bonded complex by infrared action spectroscopy. From such measurements, they estimate a binding energy of  $(D_0/hc) \leq 430 \text{ cm}^{-1}$ . However, as yet, they have no firm evidence for the promotion of reaction



to  $\text{H} + \text{CO}_2$  when these species are provided with additional vibrational energy. At the present time, the role of hydrogen bonding in the  $\text{OH} + \text{CO}$  reaction remains less than certain.

### 3. Conclusions

As discussed above, the reactions of OH with many species, especially oxygenated compounds, can proceed via the formation of complexes that involve one or two hydrogen bonds. The presence of an attractive well in the entrance channel of a potential energy surface can influence the dynamics, and hence the course, of the reaction. Its existence can manifest itself in terms of the negative temperature dependence, which is to be expected when there is an attractive encounter between reactants. Just as importantly, it can also lead to pressure dependence for the overall reaction and the generation of products that would not be expected from a simple H-atom abstraction reaction. These drastic changes arise from quite subtle changes in the topology of the entrance channel, and the extent to which the course of the reaction changes may depend on small differences in energetics and available pathways. However, the changes can have large impacts on practical systems such as the atmosphere. For example, the increase in the rate constant for the  $\text{OH} + \text{HNO}_3$  reaction at low temperatures has a major effect on the ratio of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 + \text{NO}_3$ ) to  $\text{NO}_y$  ( $\text{NO}_x + \text{HNO}_3 + \text{other nitrates and pernitrates}$ ) in the atmosphere. This change led to major revision in the efficiency of nitrogen oxides in the stratosphere toward ozone production and destruction. Therefore, quantifying the consequences of the adduct formation in OH reactions is very important.

As discussed for the  $\text{OH} + \text{HX}$  reactions, the orientation of the reagents into a favorable position by the initial interaction of the reagents could be important. In the case of the doubly bonded adducts discussed above (e.g.,  $\text{OH} + \text{HNO}_3$ ,  $\text{OH} + \text{carboxylic acids}$ , etc.) the synergistic effect of the formation of the adduct and the orientation of the reagents in the adduct could greatly enhance reactivity. In all the doubly hydrogen-bonded cases, the adduct is already "prealigned" to lead to the transition state that yields the products.

A general feature of reactions that proceed via a moderately bound collision complex appears to be the deviation from simple Arrhenius behavior. The formation of complexes arises from the presence of a potential well. The competition between collisional stabilization of the adduct, its dissociation back to reactants, and its fragmentation to reaction products may be evidenced by the complex behavior of the rate constant as a function of temperature and pressure. One would expect to see a pressure dependence of the rate constants for these reactions when redissociation of the adduct is competitive with decomposition to the products and when the adduct's lifetime with respect to these processes is sufficiently long for collisions with the bath gas to occur at experimentally attainable pressures.

Another general feature of these reactions is that the potential barrier separating the complex from the products should not be too far above the energies of the reactants nor so wide as to prevent tunneling through it. In this regard, it should be noted that transfer of a H atom, converting complex to products, is unusual and therefore important. One would not expect significant tunneling for heavier atoms (except D) and especially not for any groups of atoms.

Diagnosing the possibility of reaction via a hydrogen-bonded complex should start with the calculation of adduct structure and energetics. If the adduct stability is greater than about  $25 \text{ kJ mol}^{-1}$ , then one needs to consider the possibility of pressure dependence and negative temperature dependence. Also, the

possibility of multiple product formation should be considered. Measurement of the rate constant over a wide range of temperatures, especially lower temperatures, and pressures should help diagnose the possibility of adduct formation.

Isotopic substitution of the reagents would be another important step. A negative activation energy with a large kinetic isotope effect would indicate the role of an adduct. Identification and quantification of the products would greatly help in this process. Direct detection of the adduct would, if possible, be greatly beneficial in understanding these reactions.

The role of oxygenated hydrocarbons in the atmosphere is receiving more attention because of their role in the upper troposphere, because they are formed in the troposphere, and because they are being used as fuel additives and substitutes. Their degradation in the atmosphere is likely to be initiated, primarily, by reaction with OH. These oxygenated hydrocarbons are also reactants that might form two hydrogen bonds with OH, so the unusual temperature and pressure dependence from these reactions can be expected and needs to be investigated.

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### References and Notes

- (1) Wayne, R. P. *Chemistry of Atmospheres*, 3rd ed.; Oxford University Press: Oxford, 2000.
- (2) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.
- (3) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F., Jr.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 12*; Publication 97-4; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 1997.
- (4) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995-1996.
- (5) Legon, A. C. *Chem. Soc. Rev.* **1990**, *19*, 197.
- (6) Nesbitt, D. J. *Annu. Rev. Phys. Chem.* **1994**, *45*, 367 and references therein.
- (7) (a) Clary, D. C. *Annu. Rev. Phys. Chem.* **1990**, *41*, 61. (b) Clary, D. C.; Nyman, G.; Hernandez, R. *J. Chem. Phys.* **1994**, *101*, 3704.
- (8) Smith, I. W. M. *Kinetics and Dynamics of Elementary Gas Reactions*; Butterworths: London, 1980.
- (9) (a) Donahue, N. M.; Clarke, J. S.; Anderson, J. G. *J. Phys. Chem. A* **1998**, *102*, 3923. (b) Clarke, J. S.; Kroll, J. H.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem. A* **1998**, *102*, 9847.
- (10) Donahue, N. M. *J. Phys. Chem. A* **2001**, *105*, 1489. (b) Rypkema, H. A.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem. A* **2001**, *105*, 1498.
- (11) Smith, I. W. M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3741.
- (12) Ravishankara, A. R.; Lovejoy, E. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2159.
- (13) (a) Donahue, N. M.; Anderson, J. G.; Demerjian, K. J. *J. Phys. Chem. A* **1998**, *102*, 3121. (b) Tully, F. P.; Droge, A. T.; Koszykowski, M. L.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 691. (c) Droge, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 1949.
- (14) Tsiouris, M.; Wheeler, M. D.; Lester, M. I. *Chem. Phys. Lett.* **1999**, *302*, 192.
- (15) Wheeler, M. D.; Tsiouris, M.; Lester, M. I.; Lendvay, G. J. *Chem. Phys.* **2000**, *112*, 6590.
- (16) Atkinson, R. *Int. J. Chem. Kinet.* **1986**, *18*, 555.
- (17) Neeb, P. *J. Atmos. Chem.* **2000**, *35*, 295.
- (18) Gierczak, T.; Talukdar, R. K.; Herndon, S. C.; Vaghjiani, G. L.; Ravishankara, A. R. *J. Phys. Chem. A* **1997**, *101*, 3125.
- (19) (a) Melissas, V. S.; Truhlar, D. G. *J. Chem. Phys.* **1993**, *99*, 1013. (b) Melissas, V. S.; Truhlar, D. G. *J. Chem. Phys.* **1993**, *99*, 3542. (c) Hu, W.-P.; Liu, Y.-P.; Truhlar, D. G. *J. Chem. Soc., Faraday Trans. 2* **1994**, *90*, 1715.
- (20) Dunlop, J. R.; Tully, F. P. *J. Phys. Chem.* **1993**, *97*, 11 148.
- (21) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **1999**, *103*, 6049.
- (22) Xia, W. S.; Lin, M. C. *J. Chem. Phys.* **1982**, *114*, 4522.

- (23) (a) Smith, I. W. M.; Zellner, R. *Int. J. Chem. Kinet.* **1975**, *Sympos. 1*, 341. (b) Margitan, J. J.; Kaufman, F.; Anderson, J. G. *Int. J. Chem. Kinet.* **1975**, *Sympos. 1*, 281.
- (24) Brown, S. S.; Talukdar, R. K.; Ravishankara, A. R. *J. Phys. Chem. A* **1999**, *103*, 3031.
- (25) Brown, S. S.; Burkholder, J. B.; Talukdar, R. K.; Ravishankara, A. R. *J. Phys. Chem. A* **2001**, *105*, 1605.
- (26) Marinelli, W. J.; Johnston, H. S. *J. Chem. Phys.* **1982**, *77*, 1225.
- (27) Lamb, J. J.; Mozurkewich, M.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6441.
- (28) McCabe, D. C.; Smith, I. W. M.; Gilles, M. K.; Talukdar, R. K.; Brown, S. S.; Ravishankara, A. R., to be submitted for publication.
- (29) Smith, I. W. M.; Williams, M. D. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 1849.
- (30) (a) Baiocchi, F. A.; Klemperer, W. J. *J. Chem. Phys.* **1983**, *78*, 3509. (b) Lovas, F. J.; Suenram, R. D.; Ross, S.; Klobukowski, M. J. *Mol. Spectrosc.* **1987**, *123*, 167.
- (31) (a) Chao, J.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1978**, *7*, 363. (b) Buttner, R.; Maurer, G. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 877.
- (32) (a) Jolly, G. S.; Singleton, D. L.; Paraskevopoulos, G. *J. Phys. Chem.* **1987**, *91*, 3463. (b) Singleton, D. L.; Paraskevopoulos, G.; Irwin, R. S.; Jolly, G. S.; McKenney, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7786.
- (33) Wine, P. H.; Aсталos, R. J.; Mauldin, R. L., III. *J. Phys. Chem.* **1985**, *89*, 2620.
- (34) (a) Li, Q.; Osborne, M. C.; Smith, I. W. M. *Int. J. Chem. Kinet.* **2000**, *32*, 85. (b) Wallington, T. J.; Andino, J. M.; Ball, J. C.; Japar, S. M. *J. Atmos. Chem.* **1990**, *10*, 301.
- (35) Singleton, D. L.; Paraskevopoulos, G.; Irwin, R. S. *J. Am. Chem. Soc.* **1989**, *111*, 5248.
- (36) Koch, S.; Moortgat, G. K. *Chem. Phys. Lett.* **1990**, *173*, 531.
- (37) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **2000**, *104*, 3211.
- (38) Vasvári, V.; Szilágyi, I.; Bencsura, A.; Dobe, S.; Berces, T.; Henon, E.; Canneaux, S.; Bohr, F. *Phys. Chem. Chem. Phys.* **2001**, *3*, 551.
- (39) (a) Taylor, P. H.; Rahman, M. S.; Arif, M.; Dellinger, B.; Marshall, P. Proceedings of the Twenty-Fifth Symposium (International) on Combustion, **1996**, 497–504 (b) D'Anna, B.; Andresen, O.; Gefen, Z.; Nielsen, C. *J. Phys. Chem. Chem. Phys.* **2001**, *3*, 3057.
- (40) Alavrez-Idaboy, J. R.; Mora-Diez, N.; Boyd, R. J.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2001**, *123*, 2018.
- (41) Wollenhaupt, M.; Carl, S. A.; Horowitz, A.; Crowley, J. N. *J. Phys. Chem. A* **2000**, *104*, 2695.
- (42) Wollenhaupt, M.; Crowley, J. N. *J. Phys. Chem. A* **2000**, *104*, 6429.
- (43) Gierczak, T.; Ravishankara, A. R.; Gilles, M. K.; Bauerle, S.; Talukdar, R. K., to be submitted for publication.
- (44) Le Calve, S.; Hitier, D.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1998**, *102*, 4579.
- (45) (a) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Hurley, M. D.; Goto, M.; Kawasaki, M. *J. Phys. Chem. A* **2002**, submitted for publication.
- (b) Vandenberk, S.; Vereecken, L.; Peeters, J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 461.
- (46) Sharkey, P.; Smith, I. W. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 631.
- (47) Ravishankara, A. R.; Wine, P. H.; Wells, J. R.; Thompson, R. L. *Int. J. Chem. Kinet.* **1985**, *17*, 1281.
- (48) Battin-Leclerc, F.; Kim, I. K.; Talukdar, R. K.; Portmann, R. W.; Ravishankara, A. R.; Steckler, R.; Brown, D. *J. Phys. Chem. A* **1999**, *103*, 3237.
- (49) Steckler, R.; Thurman, G. M.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *106*, 3926.
- (50) (a) Fraser, G. T.; Pine, A. S. *J. Chem. Phys.* **1989**, *91*, 637. (b) Oudejans, L.; Miller, R. E. *J. Phys. Chem. A* **1995**, *99*, 13 670.
- (51) (a) Ravishankara, A. R.; Wine, P. H.; Langford, A. O. *Chem. Phys. Lett.* **1979**, *63*, 479. (b) Ravishankara, A. R.; Wine, P. H.; Wells, J. R. *J. Chem. Phys.* **1985**, *83*, 447.
- (52) Sims, I. R.; Smith, I. W. M.; Clary, D. C.; Bocherel, P.; Rowe, B. R. *J. Chem. Phys.* **1994**, *101*, 1748.
- (53) Atkinson, D. B.; Jaramillo, V. I.; Smith, M. A. *J. Phys. Chem. A* **1997**, *101*, 3356.
- (54) Clary, D. C.; Stoecklin, T.; Wickham, A. G. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 631.
- (55) Campuzano-Jost, P.; Crowley, J. N. *J. Phys. Chem. A* **1999**, *103*, 2712.
- (56) Brunning, J.; Derbyshire, D. W.; Smith, I. W. M.; Williams, M. D. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 105.
- (57) Frost, M. J.; Sharkey, P.; Smith, I. W. M. *J. Phys. Chem.* **1993**, *97*, 12 254.
- (58) (a) Forster, R.; Frost, M.; Fulle, D.; Hamann, H. F.; Hippler, H.; Schlegel, A.; Troe, J. *J. Chem. Phys.* **1995**, *103*, 2949. (b) Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J. *J. Chem. Phys.* **1996**, *105*, 983.
- (59) Schatz, G. C.; Fitzcharles, M. S.; Harding, L. B. *Faraday Discuss. Chem. Soc.* **1987**, *84*, 349.
- (60) (a) Lester, M. I.; Pond, B. V.; Anderson, D. T.; Harding, L. B.; Wagner, A. F. *J. Chem. Phys.* **2000**, *113*, 9889. (b) Lester, M. I.; Pond, B. V.; Marshall, M. D.; Anderson, D. T.; Harding, L. B.; Wagner, A. F. *Faraday Discuss. Chem. Soc.* **2000**, *118*, 000.
- (61) Kudla, K.; Koures, A. G.; Harding, L. B.; Schatz, G. C. *J. Chem. Phys.* **1992**, *96*, 7465.
- (62) Dr. G. B. Ellison has pointed out to us that, in the reactions of OH with carbonyl compounds, in addition to hydrogen-bonding one may have to consider the effects of orbital symmetry on reactivity. In brief, when OH forms a hydrogen bond with a carbonyl compound, the odd electron in the p orbital on the oxygen atom of the OH may be oriented in or perpendicular to the “carbonyl plane” (in the case of H<sub>2</sub>CO...HO, these surfaces could be designated <sup>2</sup>A' and <sup>2</sup>A''). At least for rigid complexes, this would mean that reaction on one surface would be much favored over that on the other. However, given the nonrigidity of the complexes and the energy that is released as the complexes form from reagents, such differences between reaction on the two surfaces are likely to be reduced in practice. These effects are therefore ignored in the discussion in this section.