

Complexes of Hydroperoxyl Radical with Glyoxal, Methylglyoxal, Methylvinyl Ketone, Acrolein, and Methacrolein: Possible New Sinks for HO₂ in the Atmosphere?

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Structures and energetics of complexes of HO₂ with glyoxal, methylglyoxal, methylvinyl ketone, and methacrolein have been calculated using density functional theory. The hydroperoxy radical was found to form strong hydrogen bonds with glyoxal, methylglyoxal, methylvinyl ketone, acrolein, and methacrolein. Binding energies D_0 for these complexes were as high as 10.9 kcal mol⁻¹ for HO₂-methylvinyl ketone. Vibrational frequencies are presented for monomers and complexes. Equilibrium constants for the formation of some of these complexes are also calculated. As a result, it is predicted that the strongest of these complexes, the hydroperoxy radical-methylvinyl ketone complex, should exist in the atmosphere under certain conditions.

I. Introduction

Recent field measurements¹ and models of HO_x at Oki Island in Japan show that, under certain conditions, the concentration of hydroperoxyl radical (HO₂) is often overestimated when compared to models containing the known chemistry of HO_x in the troposphere. The authors propose that a possible explanation is a missing HO_x sink. Furthermore, they see a strong correlation between the missing sink of HO₂ and the modeled concentration of carbonyl-containing organics, namely, glyoxal (H₂C₂O₂). This led to the proposal that the missing sink may involve a reaction between HO₂ and carbonyl-containing compounds. The hydroperoxyl radical is known to react with both formaldehyde (HCHO)² and glyoxal.³ The rate constant for the reaction of HO₂ with formaldehyde has been determined to be on the order of 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹, while with glyoxal the rate is somewhat faster, on the order of 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹. Both of these reactions are relatively slow and considered of marginal importance under most atmospheric conditions.⁴ Furthermore, both reactions likely proceed via an adduct intermediate.⁵ There are little data from studies of the reactions of the hydroperoxyl radical with higher order carbonyl-containing compounds. Kanaya et al.¹ report that methacrolein (CH₂=C(CH₃)CHO) and methyl vinyl ketone (CH₂=CHCOCH₃) are likely to be present at high concentrations at the Oki site. In previous works,^{6,7} we have theoretically investigated the reactions of HO₂ with carbonyl-containing compounds to form adducts, namely, with formaldehyde, acetaldehyde (CH₃CHO), and acetone (CH₃COCH₃), as well as with formic acid (HCO₂H) and acetic acid (CH₃CO₂H). In the former work, we find that acetaldehyde and acetone form more strongly bound adducts with HO₂ than with formaldehyde does. This led us, like Kanaya et al., to postulate the possible importance of a reaction between HO₂ and these species. In this work, we examine the adduct-forming reactions of HO₂ with the carbonyl-containing compounds implicated in the field measurements, glyoxal, methacrolein, and methyl vinyl ketone, along with methyl glyoxal (CH₃COCHO) and acrolein (CH₂=CHCHO).

II. Computational Methods

All calculations were performed using the GAUSSIAN 94⁸ suite of programs. Geometries were optimized using the Becke three-parameter hybrid functional combined with Lee, Yang, and Parr correlation [B3LYP]⁹ density functional theory method. In our previous work involving complexes of organic molecules and water,^{7,10} energetics, structure, and frequency shifts calculated compared favorably to experimental data.^{11–14} The largest basis sets employed is the 6-311++G (3df,3pd). Frequency calculations were also performed at this level of theory. Zero-point energies were taken from the same level of theory for calculations of the binding energy D_0 . Zero-point energies taken from these frequency calculations can be assumed to be an upper limit due to the anharmonic nature of the potential energy surface.¹⁵ Recent studies^{16,17} show that these methods agree reasonably well with the experimental data, as well as with more costly ab initio methods, available for a large number of carbonyl-containing species in terms of structures, energetics and vibrational frequencies. In an excellent comparison article, Rablen et al.¹⁸ showed that the B3LYP method provides data that is in good agreement with MP2 methods, provided a large basis set is used. In that work, smaller basis sets were employed than in this one, but the BSSE was generally on the order of 1 kcal mol⁻¹.

III. Results and Discussion

We have examined complexes of several oxygen-containing organic compounds with the hydroperoxyl radical (HO₂). The organics studied are glyoxal (GLY), methylglyoxal (MGLY), acrolein (ACR), methacrolein (MACR), and methyl vinyl ketone (MVK). When compared to our previous studies of HO₂ complexes with formaldehyde, acetaldehyde, and acetone, as well as our more recent study of HO₂ with formic and acetic acid, these results start to show some interesting trends. The complexes in this study are shown in Figure 1. There are a few common characteristics that are seen. In all the complexes, the oxygen on the carbonyl group acts as the hydrogen acceptor of for the HO₂. This is similar to what was seen for the previously studied organics. There is also a second, weaker interaction

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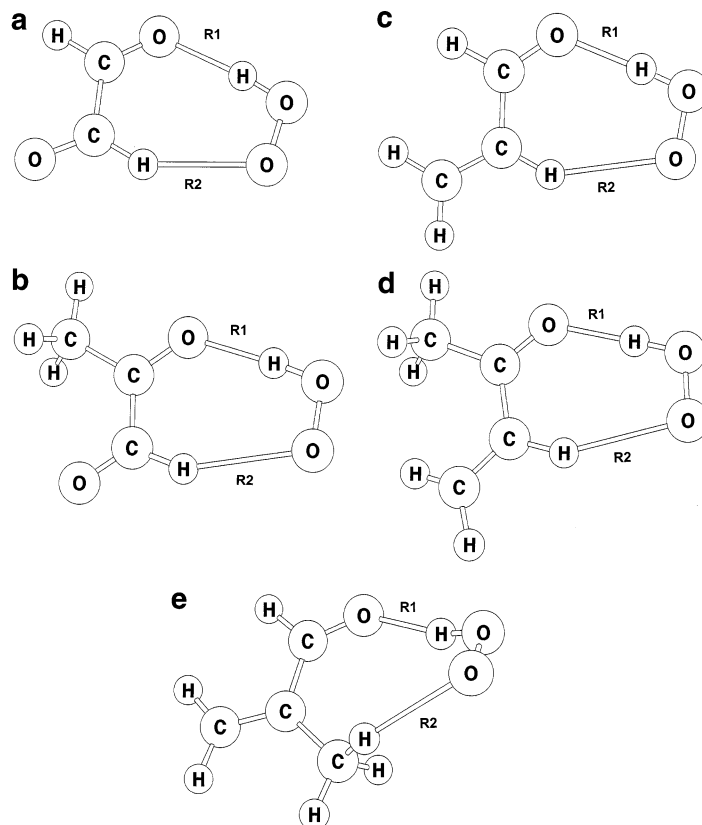


Figure 1. HO₂-organic carbonyl compounds: (a) HO₂-glyoxal, (b) HO₂-methylglyoxal, (c) HO₂-methylvinyl ketone, (d) HO₂-acrolein, (e) HO₂-methacrolein.

TABLE 1: Selected Geometric Parameters for the HO₂ Complexes^a

organic species	B3LYP/6-311++G(3df,3pd)						ref
	R1	R2	C=O		O-H		
			δ	δ	δ		
formaldehyde	1.777	2.719	1.206	+0.3	0.990	+1.5	6
acetaldehyde	1.734	2.736	1.213	+0.8	0.993	+1.9	6
acetone	1.709	2.449	1.219	+0.8	0.996	+2.2	6
glyoxal	1.817	2.453	1.206	+0.5	0.987	+1.2	this work
methyl glyoxal	1.775	2.453	1.215	+0.6	0.990	+1.5	this work
acrolein	1.725	2.431	1.218	+0.8	0.995	+2.1	this work
methacrolein	1.748	2.504	1.215	+0.6	0.990	+1.5	this work
methyl vinyl ketone	1.705	2.400	1.225	+0.8	0.997	+2.3	this work
formic acid	1.639	1.736	1.217	+1.8	1.011	+3.7	7
acetic acid	1.608	1.724	1.224	+2.4	1.015	+4.1	7

^a All bond distances are reported in angstroms. δ is the percent difference for the complex versus the isolated monomer.

between the terminal oxygen of HO₂ and one of the hydrogen atoms on the organic species. For all the complexes examined in this study, the former interaction is stronger than the latter. This was also observed in our former studies of aldehydes, ketones, and even of carboxylic acids.

Some key geometric parameters for these complexes are shown in Table 1. The primary hydrogen bond distances are in the following order from shortest to longest: MVK < ACR < MACR < MGLY < GLY. Not surprisingly, this is also the order of stability of the HO₂ complexes with these organics. When this coordinate is compared to the ketones and aldehydes previously studied, methyl vinyl ketone still has the strongest bond in this coordinate, with a slightly shorter distance than the acetone complex. The same coordinate in the acetaldehyde complex falls between acrolein and methacrolein, while in the formaldehyde complex, it is between methyl glyoxal and

glyoxal. In the carboxylic acid complexes, this hydrogen bond distance is considerably shorter than that in any of the other species. It is interesting that in all of these species, the hydrogen bond is between a carbonyl group and the hydrogen of HO₂, but the range of this hydrogen bond is over 0.2 Å, about 12% of the mean distance of these hydrogen bonds. The strength of this hydrogen bond is clearly very dependent on what is bonded to the carbonyl group. That is what kind of oxygenated organics we are talking about. There are some trends that can be seen. The organics can be divided into three distinct groups, at least from this small data set. Taking this coordinate alone into account, the order of hydrogen bond strength seems to be carboxylic acid > ketone > aldehyde. The carbonyl-accepting hydrogen bond affects two coordinates mostly. One is the hydrogen-oxygen bond distance on the hydroperoxyl radical. The elongation of this bond is related to the strength of the adjacent hydrogen bond. In the carboxylic acid complexes, this bond is elongated by 4.1% for acetic acid, and 3.7% for formic acid. But even for the glyoxal complex, which has the weakest hydrogen bond, this bond is elongated by 1.2%. The other complexes fall between these numbers, with elongations of 2.3% for MVK, 2.1% for ACR, and 1.5% for MACR and MGLY. The other coordinate most affected by this hydrogen bond is along the carbon-oxygen double bond on the organic species. This bond is also longer in the complex than that in the isolated monomer, however, to a lesser extent than the O-H bond in HO₂. Only in the carboxylic acids is the elongation over 1%. Also, the magnitude of this elongation is not as strictly dependent on the length of the adjacent hydrogen bond. Of the examples presented, this is most notable in comparing the formaldehyde complex to the glyoxal complex. While the hydrogen bond distance is shorter in the formaldehyde complex, the elongation of the C=O is 0.3% compared to 0.5% in the

glyoxal complex, although the absolute value of this bond distance is the same. This is because there are more factors affecting the C=O bond distance in a variety of organics than the O–H bond distance in HO₂. For this reason, it is not wise to estimate the strength of the hydrogen bond solely on the basis of the degree of elongation of the carbonyl bond, e.g., the red shift of the C=O stretch.

In all of the complexes studied in this work, there is a secondary interaction between the terminal oxygen of the HO₂ and a hydrogen atom of the organic species. This work gives new insight into this weaker interaction better than our previous studies, so we will include some new insight into those works as well. In the carboxylic acids, there is a second hydrogen bond formed between the terminal oxygen of HO₂ and the acidic hydrogen of the acid. The distance for this coordinate is comparable, but not shorter than the primary hydrogen bond. For the other species, we hesitate to call these interactions hydrogen bonds. However, it is clear that there is an interaction and that it affects the binding energies of these complexes. The next strongest interactions in this coordinate are for the complexes of methyl vinyl ketone and of acrolein. These species both share the next strongest hydrogen acceptor group, an α -hydrogen that is adjacent to a carbon–carbon double bond. It makes sense that this hydrogen would be a relatively good electron acceptor. The next shortest bond distance in this coordinate is in the acetone complex with the hydroperoxyl radical, followed by complexes of glyoxal and methyl glyoxal. In the acetone complex, the hydrogen donor group is a methyl group, while in the glyoxal species it is the hydrogen adjacent to the carbonyl group, the acyl hydrogen. Of the molecules studied in this work, the longest secondary interaction coordinate is in the methacrolein complex, in which the hydrogen donor is a methyl group. Why is the hydrogen donor not the acyl hydrogen, as was the case for the preceding two molecules? This is in contrast to what is seen in acetaldehyde, for example. It seems that this hydrogen and a methyl group hydrogen are similar in terms of being electron acceptors. The surrounding groups of these species influence which will be a better hydrogen donor. Hence in acetone, the methyl group is a better hydrogen donor than the acyl hydrogen atoms in either glyoxal or methyl glyoxal. Whereas in methacrolein the methyl hydrogen is a weaker donor than that in those two molecules, the methyl hydrogen is stronger than its own acyl hydrogen, and stronger than that of formaldehyde and acetaldehyde. In acetaldehyde, the methyl hydrogen is not as good a donor as the acyl hydrogen on that same carbonyl group. So in our small data set so far, the order of strength of hydrogen donors on organic molecules seems to be acidic O–H > α -hydrogen > methyl group hydrogen \approx acyl hydrogen.

The calculated harmonic vibrational frequencies and intensities are reported in Table 2. Each species has $3N - 6$ vibrational frequencies. Complexation results in the appearance of new intermolecular modes, mostly at lower energies. The vibrational frequencies here are reported to assist the interpretations of experimental studies in identifying these complexes. It can be seen that there are a few modes with quite large calculated band intensities. We will focus on three of these modes; two intramolecular and one intermolecular. The first is the O–H stretch on the hydroperoxyl radical. In each complex, this mode has the largest calculated intensity. The isolated monomer has a calculated frequency of 3605 cm⁻¹ and an intensity of 344.2 km mol⁻¹ at this level of theory. In each of these complexes, this coordinate is elongated; hence, the vibrational frequency is red shifted. This effect ranges from 192 cm⁻¹ in the HO₂-

TABLE 2: Calculated Harmonic Vibrational Frequencies and Intensities of the HO₂ Complexes

B3LYP/6-311++G(3df,3pd)									
glyoxal		methyl glyoxal		acrolein		methacrolein		mvk	
<i>v</i>	<i>I</i>	<i>v</i>	<i>I</i>	<i>v</i>	<i>I</i>	<i>v</i>	<i>I</i>	<i>v</i>	<i>I</i>
3410	623.5	3355	859.8	3258	997.0	3345	928.7	3231	1.5
2983	2.5	3158	3.9	3230	3.9	3227	3.7	3215	1232.0
2982	57.8	3094	0.3	3166	2.4	3139	3.8	3155	3.9
1799	55.6	3043	0.9	3137	4.7	3123	7.4	3151	4.9
1788	197.0	2971	7.8	2949	87.5	3087	7.3	3147	3.8
1538	56.5	1803	92.4	1740	382.5	3035	6.9	3100	3.1
1390	2.2	1766	237.0	1675	3.7	2948	79.9	3043	2.2
1347	8.7	1553	52.1	1575	57.2	1743	405.6	1714	305.7
1201	18.4	1458	10.7	1466	9.7	1684	9.7	1679	30.5
1092	0.0	1453	19.9	1394	13.1	1550	35.0	1586	54.3
1062	0.1	1398	46.6	1312	1.1	1500	23.9	1478	10.5
828	5.5	1384	0.2	1208	20.1	1480	10.9	1474	3.1
609	109.0	1251	15.4	1200	40.2	1462	0.4	1455	35.8
551	0.3	1203	17.1	1062	14.4	1428	7.2	1396	38.0
358	55.6	1090	4.2	1043	2.0	1403	3.3	1337	1.2
209	6.3	1015	2.2	1018	36.6	1336	38.4	1295	76.0
140	9.4	919	0.1	937	20.3	1203	15.8	1208	14.0
137	4.7	784	10.9	717	115.4	1082	0.6	1084	3.7
82	10.9	653	105.4	623	0.4	1048	24.9	1072	14.0
80	2.2	575	27.5	586	5.5	1022	0.8	1055	2.1
46	8.5	498	26.0	349	21.3	993	32.1	1014	37.1
		473	0.0	238	41.5	985	10.9	962	16.7
		256	14.6	187	1.3	832	16.7	778	2.4
		212	34.5	159	1.5	708	0.1	744	97.8
		141	1.6	105	0.0	643	70.9	699	5.0
		136	11.6	85	4.6	626	29.2	553	9.2
		97	9.6	54	1.0	445	9.2	511	19.3
		82	1.4			417	5.8	445	0.8
		56	0.3			282	10.9	290	2.5
		33	0.0			215	27.0	237	41.7
						207	8.8	157	1.1
						181	3.6	144	0.5
						131	1.5	121	0.3
						83	1.7	87	3.9
						47	0.6	60	0.7
						38	1.0	45	0.5

^a *v* is the calculated frequency in cm⁻¹. *I* is the intensity in km mol⁻¹. Frequencies in boldface are discussed in the text.

Glyoxal complex to 387 cm⁻¹ in the HO₂-MVK complex. In the methyl vinyl ketone complex, this mode is actually lower in energy than a calculated C–H stretch in that molecule. In addition, the intensity of the O–H stretching mode increases by nearly a factor of 2 in the glyoxal complex, and nearly a factor of 4 in the MVK complex. The other complexes exhibit this effect somewhere between these two, according to the strength of their hydrogen bonds. The second mode we will examine is the carbonyl C=O stretch. This mode is calculated to be between 1700 and 1800 cm⁻¹ for these complexes. In each of these complexes, this mode is red shifted due to the elongation of this coordinate. It also has a large calculated band intensity. This mode would be a good candidate for experimental detection. For formic and acetic acid, the monomer is easily distinguished from the dimer using this mode. The third mode we will discuss is an intermolecular mode. It should be noted that for the more strongly bound complexes especially, there is a degree of coupling between inter- and intramolecular modes. Many of the intermolecular modes do not have very strong calculated intensities. In each case studied here, there is an exception involving the hydrogen of the hydroperoxyl radical, along the R1 coordinate. This mode is calculated at 609 cm⁻¹ for the glyoxal complex, at 653 cm⁻¹ for the methyl glyoxal complex, 717 cm⁻¹ for the acrolein complex, 643 cm⁻¹ for the methacrolein complex, and 744 cm⁻¹ for the methyl vinyl ketone complex. Note that it increases in energy with increasing

TABLE 3: Binding Energies of the HO₂ Complexes^a

organic	B3LYP/6-311++G(3df,3pd)	
	D_e	D_0
glyoxal	7.1	5.1
methyl glyoxal	8.1	6.2
acrolein	10.3	8.2
methacrolein	9.1	7.1
methyl vinyl ketone	10.9	8.9

^a Energies reported in kcal mol⁻¹.

hydrogen bond strength. Due to the relatively strong calculated intensity, and the fact that it is an intermolecular mode, the authors feel that this is another good candidate for detection.

The binding energies for the complexes studied in this work are given in Table 3. Included in this table are the binding energies of carbonyl-containing compounds and HO₂ from our previous works. All binding energies are computed at the B3LYP/6-311++G(3df,3pd) level of theory. Of the organics examined in this study, the strongest binding energy was for the complex of HO₂ with methyl vinyl ketone with a well depth D_e of 10.9 kcal mol⁻¹ and a binding energy D_0 of 8.9 kcal mol⁻¹. This is in-line with the structure of the complex in that the primary hydrogen bond is with a ketonic carbonyl group, which was found to be a better hydrogen acceptor than the carbonyl group of an aldehyde in our previous works. Interestingly, the binding energy for the HO₂-acetone complex is also 8.9 kcal mol⁻¹. The HO₂-MVK complex also has a relatively strong secondary interaction between the α -hydrogen of the organic and the terminal oxygen of the hydroperoxyl radical.

The next most strongly bound complexes are of HO₂ with acrolein ($D_e = 10.3$ kcal mol⁻¹; $D_0 = 8.2$ kcal mol⁻¹) and methacrolein ($D_e = 9.1$ kcal mol⁻¹; $D_0 = 7.1$ kcal mol⁻¹). This reflects the weaker hydrogen-accepting capability of the carbonyl group of an aldehyde than of a ketone. The difference in binding energy between these two organic complexes is probably the result of the secondary interaction between HO₂ and the organic. In acrolein, the hydrogen being donated in this interaction is an α -hydrogen, while in methacrolein it is a methyl group hydrogen. The binding energies of these HO₂ complexes are similar in magnitude to that of acetaldehyde ($D_e = 9.6$ kcal mol⁻¹; $D_0 = 7.8$ kcal mol⁻¹).

The most weakly bound complexes we present in this work are the ones of HO₂ with glyoxal ($D_e = 7.1$ kcal mol⁻¹; $D_0 = 5.1$ kcal mol⁻¹) and methyl glyoxal ($D_e = 8.1$ kcal mol⁻¹; $D_0 = 6.2$ kcal mol⁻¹). The presence of two carbonyl groups side-by-side explains why these organics have the lowest binding energies in this study. The adjacent carbonyl group acts as an electron-withdrawing group from the hydrogen-accepting carbonyl group, making the hydrogen bond weaker. The methyl glyoxal complex is more strongly bound because the carbonyl group accepting the hydrogen bond is also adjacent to a methyl group. An adjacent methyl group makes the carbonyl group a better hydrogen acceptor than an acyl hydrogen. In both of these species, the secondary interaction is between an acyl hydrogen on the organic and the terminal oxygen of the hydroperoxyl radical.

We calculated the equilibrium constant for the formation of two of these complexes using methods described in a previous work.¹⁹ The equilibrium constants were calculated for HO₂-GLY and HO₂-MVK. These are the most strongly and most weakly bound complexes studied in this work. As mentioned earlier, Kanaya et al. report¹ a correlation between glyoxal concentration and a missing HO₂ sink, and they speculate that large concentrations of methyl vinyl ketone at the Oki Island

site exist. We calculate the value of the equilibrium constant for HO₂-GLY to be 5.5×10^{-21} cm³ molecule⁻¹ at 300 K. On the basis of this equilibrium constant, as well as the measurements and calculated data (10^8 molecule cm⁻³ HO₂ and 10^6 molecule cm⁻³ glyoxal) of Kanaya et al.¹, this results in a negligible amount of HO₂-GLY in the atmosphere. We calculate an equilibrium constant for the HO₂-MVK complex to be 2.4×10^{-20} cm³ molecule⁻¹ at 300 K. Again, given the number density of MVK reported by Kanaya et al.¹ (10^7 molecule cm⁻³), the concentration of complex is negligible. These data indicate that the formation of the equilibrium complex as a sink for HO₂ is unlikely. It should be pointed out that formation of an equilibrium complex may only be the first step in a reaction process between the two species. For example, Benson²⁰ showed that the equilibrium constant for the reaction of HO₂ with formaldehyde is 4000 times larger than that with acetone. This is despite the larger equilibrium constant for the first step in this reaction process, presumably formation of a complex, is larger for acetone than for formaldehyde. A possible explanation for this is the existence of a larger barrier to formation of products postcomplex formation for HO₂-acetone than for HO₂-formaldehyde. In fact, recent work shows that the reactions of HO₂ with some ketones are very slow,²¹ and probably not significant in the atmosphere.

IV. Conclusions

We have calculated the geometry and energy of complexes of several oxidized organic species with the hydroperoxyl radical. The complexes have the general feature of forming double hydrogen bonds with HO₂. The stabilization energies of these species are relatively high compared to other complexes. Measurements show that many types of oxygenated organics are present in substantial quantities in the atmosphere; however, our calculated equilibrium constants show that these species are not directly possible as missing sinks for HO₂.

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