SUPPLEMENTARY INFORMATION

Mechanisms of Scavenging Superoxide, Hydroxyl, Nitrogen Dioxide and Methoxy Radicals by Allicin: Catalytic Role of Superoxide Dismutase in Scavenging Superoxide Radical

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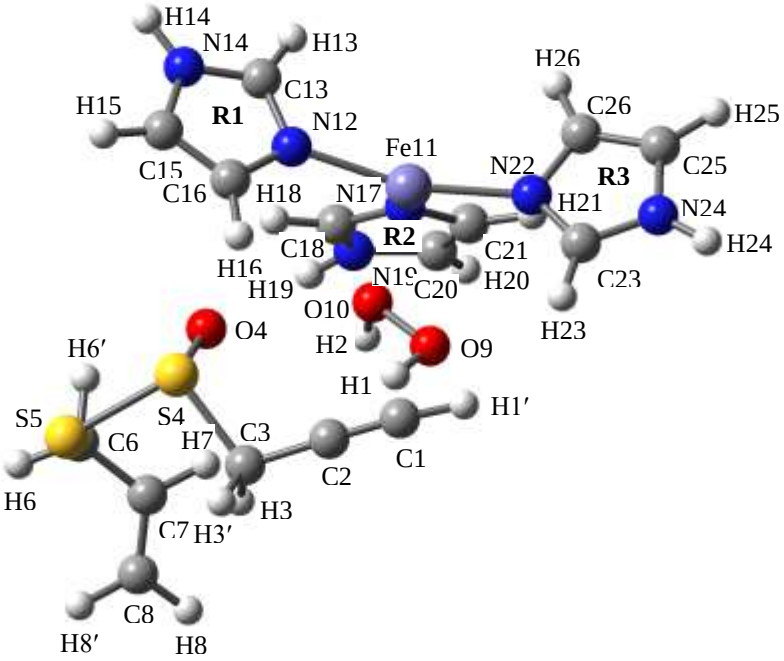
Parameters

Fe11N12=2.02 Å
Fe11N17=1.97 Å
Fe11N22=2.02 Å
O9O10=1.42 Å
Fe11O9=2.87 Å
Fe11O10=2.01 Å
C1O9=3.36 Å
C2O10=3.38 Å

Charges

R1= 0.200
R2= 0.202
R3= 0.199
Fe11= 1.194
H_2O_2= 0.148
AL_{n-2}= 0.282



(a) PC1

Parameters

Fe11N12=2.02Å
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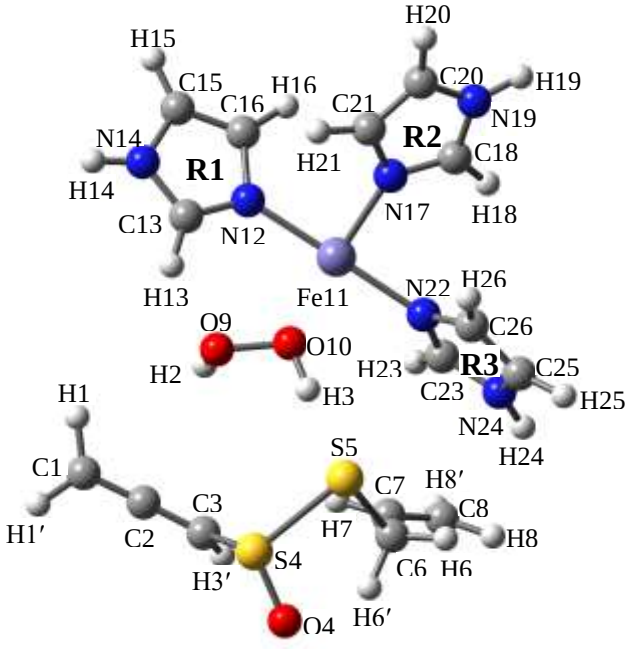
Fe11O10=2.03Å
C3H3=3.41Å
O10H3=1.00Å
C2O9=3.23Å

Charges

R1= 0.198
R2= 0.209
R3= 0.195
Fe11= 1.238
H_2O_2= 0.054
AL_{n-2}= 0.109



(b) PC2

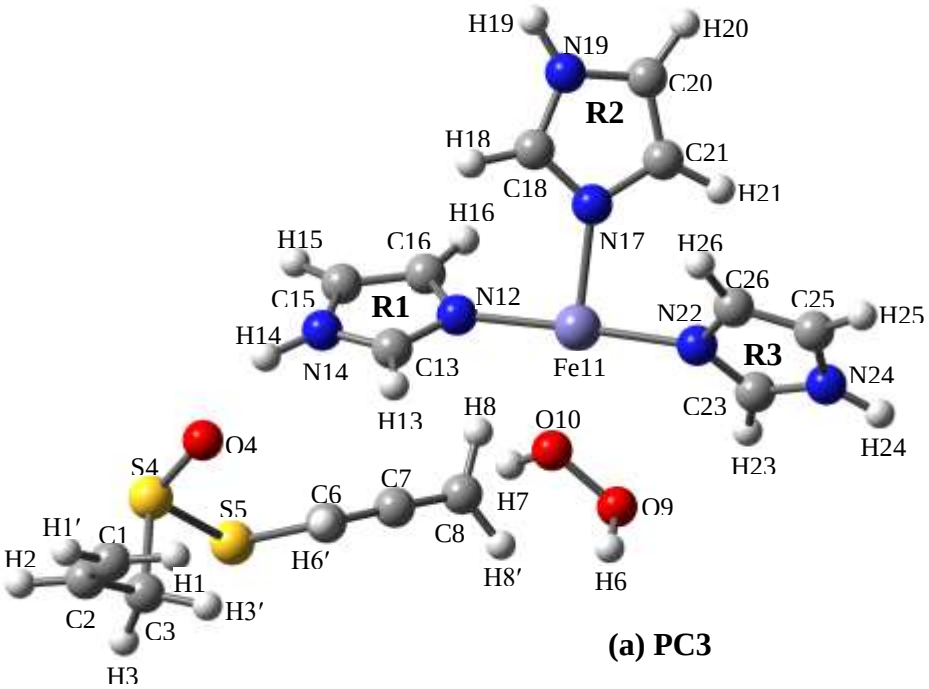
Figure S1. Optimized geometries of the product complexes ((a) PC1, (b) PC2) obtained by double hydrogen atom transfer from the (C1,C2) and (C2,C3) pairs of sites of allicin to superoxide radical anion in presence of Fe-SOD respectively. Some important bond length (Å) and total net charges at the different rings (R1-R3), allicin (-2H), Fe cation and H_2O_2 obtained at the M06-2X/6-311+G(d) level of theory in aqueous media are given.

Parameters

Fe11N12=2.01Å
Fe11N17=2.01Å
Fe11N22=2.02Å
O9O10=1.41Å
Fe11O9=2.99Å
Fe11O10=2.03Å
C7H7=2.34Å
O10H7=0.99Å
C7O10=3.31Å

Charges

R1= 0.168
R2= 0.211
R3= 0.197
Fe11= 1.241
H_2O_2= 0.126
AL_{n-2}= 0.058



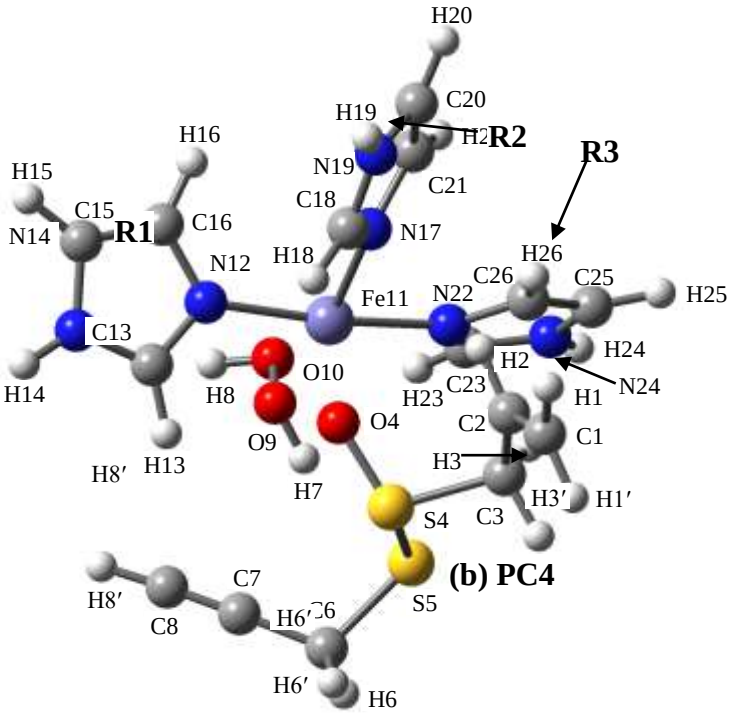
(a) PC3

Parameters

Fe11N12=2.02Å
Fe11N17=2.03Å
Fe11N22=2.06Å
O9O10=1.42Å
Fe11O9=2.82Å
Fe11O10=2.05Å
C7H7=4.46Å
O9H7=0.97Å
C8H8=2.97Å
O10H8=0.98Å

Charges

R1= 0.228
R2= 0.221
R3= 0.209
Fe11= 0.941
H_2O_2= 0.159
AL_{n-2}= 0.238



(b) PC4

Figure S2. Optimized geometries of product complexes ((a) PC3, (b) PC4) obtained by double hydrogen atom transfer from the (C6,C7) and (C7,C8) pairs of sites of allicin to superoxide radical anion in presence of Fe-SOD respectively. Some important bond lengths (Å) and total net charges at the different rings (R1-R3), allicin (-2H), Fe cation and H_2O_2 obtained at the M06-2X/6-311+G(d) level of theory in aqueous media are given.

Table S1. Barrier (ΔH^b) and released energies (ΔH^r) at 298.15 K (kcal/mol) in terms of enthalpy, involved in hydrogen atom transfer from different sites of allicin to $OH^{\cdot}$, $NO_2^{\cdot}$ and $OCH_3^{\cdot}$ obtained at the M062X/6-311+G(d) level of density functional theory in gas phase and aqueous media.[a]

[a]Results obtained in aqueous media are given in parentheses.

Sl. No.	Reaction Site	$OH^{\cdot}$		$NO_2^{\cdot}$		$OCH_3^{\cdot}$	
		(ΔH^b)	(ΔH^r)	(ΔH^b)	(ΔH^r)	(ΔH^b)	(ΔH^r)
1	C1	7.01 (7.19)	-11.23 (-11.39)	34.47 (33.75)	-3.13 (-3.02)	15.17 (4.65)	-6.61 (-4.29)
2	C2	4.38 (6.06)	-14.28 -13.97	29.66 (29.62)	-4.90 (-4.60)	10.89 (13.52)	-9.46 (-9.15)
3	C3	0.15 (1.38)	-31.86 (-34.70)	21.46 (21.29)	-18.40 (-17.81)	7.89 (31.35)	-26.48 (-48.06)
4	C6	0.72 (2.07)	-42.02 (-39.89)	18.77 (18.96)	-16.73 (-16.76)	2.72 (4.48)	-23.20 (-24.08)
5	C7	0.12 (2.07)	-13.08 (-13.90)	28.50 (29.31)	-4.87 (-5.33)	11.70 (12.28)	-11.08 (-10.34)
6	C8	5.23 (6.03)	-12.06 (-11.90)	32.46 (32.58)	-4.86 (-4.26)	13.49 (14.46)	-5.68 (-6.75)

Table S2. Barrier (ΔS^b) and released energies (ΔS^r) at 298.15 K (kcal/mol-K) in terms of entropy, involved in hydrogen atom transfer from different sites of allicin to $OH^{\cdot}$, $NO_2^{\cdot}$ and $OCH_3^{\cdot}$ obtained at the M062X/6-311+G(d) level of density functional theory in gas phase and aqueous media.[a]

Sl. No.	Reaction Site	$OH^{\cdot}$		$NO_2^{\cdot}$		$OCH_3^{\cdot}$	
		(ΔS^b)	(ΔS^r)	(ΔS^b)	(ΔS^r)	(ΔS^b)	(ΔS^r)
1	C1	-0.03 (-0.03)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)
2	C2	-0.03 (-0.03)	0.01 (0.01)	-0.03 (-0.03)	0.00 (0.00)	-0.04 (-0.04)	0.01 (0.01)
3	C3	-0.03 (-0.03)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)	-0.02 (-0.02)	0.01 (0.01)
4	C6	-0.03 (-0.03)	0.00 (0.00)	-0.04 (-0.04)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)
5	C7	-0.03 (-0.03)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)	-0.04 (-0.04)	0.01 (0.01)
6	C8	-0.03 (-0.03)	0.01 (0.01)	-0.04 (-0.03)	0.00 (0.00)	-0.04 (-0.04)	0.01 (0.01)

Table S3. NBO charges at different atoms of allicin obtained at M06-2X/6-311+G(d) level of theory in aqueous media.[a]

Sl. No.	Atoms	NBO Charge	Total
1	C1	-0.340	Total positive NBO charge= 3.303
2	H1	0.199	
3	H1′	0.203	
4	C2	-0.241	
5	H2	0.217	Total negative NBO charge= -3.304
6	C3	-0.593	
7	H3	0.249	
8	H3′	0.234	
9	S4	1.103	
10	O4	-0.979	
11	S5	0.001	
12	C6	-0.566	Net charge= -0.001
13	H6	0.258	
14	H6′	0.236	
15	C7	-0.215	
16	H7	0.204	
17	C8	-0.370	
18	H8	0.194	
19	H8′	0.203	

[a]Optimized geometry of allicin and some important bond lengths and dihedral angles are shown in Figure 1.

Table S4. NBO charges at different atoms of TS1 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C1 and C2 sites of allicin forming the product complex PC1 in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	0.150	Allicin Charge= (-2.983)+ (3.271) =0.288	27	N14	-0.521	Ring1 Charge= (-1.193)+ (1.409)=0.216
2	H1′	0.266		28	H14	0.448	
3	C2	-0.335		29	C15	-0.052	
4	C3	-0.548		30	H15	0.241	
5	H3	0.281		31	C16	-0.065	
6	H3′	0.258		32	H16	0.229	
7	S4	1.093		33	N17	-0.563	Ring2 Charge= (-1.197)+ (1.417)=0.220
8	O4	-0.953		34	C18	0.262	
9	S5	0.120		35	H18	0.231	
10	C6	-0.534		36	N19	-0.518	
11	H6	0.246		37	H19	0.450	
12	H6′	0.242		38	C20	-0.053	
13	C7	-0.233		39	H20	0.242	
14	H7	0.211		40	C21	-0.063	
15	C8	-0.340		41	H21	0.232	
16	H8	0.206		42	N22	-0.590	Ring3 Charge= (-1.217)+ (1.430)=0.213
17	H8′	0.198		43	C23	0.266	
18	O9	-0.379	Charge= (-0.871)+ (0.905)= 0.034	44	H23	0.233	
19	H1	0.508		45	N24	-0.515	
20	O10	-0.492		46	H24	0.452	
21	H2	0.397		47	C25	-0.048	
23	Fe11	0.990	0.990	48	H25	0.245	
24	N12	-0.555		49	C26	-0.064	
25	C13	0.257		50	H26	0.234	
26	H13	0.234		Net Charge=2.001			

[a]Optimized geometry of TS1 and some important bond lengths (Å) and total net charges at the different components of TS1 are shown in Figure 3 (a).

Table S5. NBO charges at the different atoms of the product complex PC1 in presence of Fe-SOD involved in double hydrogen atom transfer to superoxide radical anion from the C1 and C2 sites of allicin in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.264	Allicin	27	N14	-0.508	Ring1 Charge= (-1.230)+ (1.447)=0.217
2	H1′	0.259		28	H14	0.449	
3	C2	-0.013		29	C15	-0.020	
4	C3	-0.662	Charge= (-3.044)+ (3.097) =0.053	30	H15	0.256	
5	H3	0.293		31	C16	-0.075	
6	H3′	0.271		32	H16	0.231	
7	S4	1.066		33	N17	-0.623	Ring2 Charge= (-1.204)+ (1.420)=0.216
8	O4	-1.001		34	C18	0.254	
9	S5	0.090		35	H18	0.230	
10	C6	-0.535		36	N19	-0.505	
11	H6	0.253		37	H19	0.450	
12	H6′	0.250		38	C20	-0.023	
13	C7	-0.264		39	H20	0.255	
14	H7	0.207		40	C21	-0.053	
15	C8	-0.307		41	H21	0.231	
16	H8	0.208		42	N22	-0.601	Ring3 Charge= (-1.192)+ (1.444)=0.252
17	H8′	0.200		43	C23	0.248	
18	O9	-0.411	Charge= (-0.885)+ (1.031)= 0.146	44	H23	0.236	
19	H1	0.492		45	N24	-0.499	
20	O10	-0.474		46	H24	0.476	
21	H2	0.539		47	C25	-0.025	
23	Fe11	1.116	1.116	48	H25	0.251	
24	N12	-0.627		49	C26	-0.067	
25	C13	0.271		50	H26	0.233	
26	H13	0.240		Net Charge=2.000			

[a]Optimized geometry of PC1 and some important bond lengths (Å) and total net charges at the different components of PC1 are shown in Figure S1 (a).

Table S6. NBO charges at different atoms of TS2 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C2 and C3 sites of allicin forming the product complex PC2 in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.464	Allicin	27	N14	-0.521	Ring1 Charge= (-1.204)+ (1.413)=0.209
2	H1	0.300		28	H14	0.448	
3	H1′	0.298		29	C15	-0.058	
4	C2	0.345		30	H15	0.241	
5	C3	-0.713	Charge= (-3.194)+ (3.653) =0.459	31	C16	-0.062	
6	H3′	0.292		32	H16	0.229	
7	S4	1.207		33	N17	-0.564	Ring2 Charge= (-1.191)+ (1.410)=0.219
8	O4	-0.915		34	C18	0.254	
9	S5	0.103		35	H18	0.233	
10	C6	-0.535		36	N19	-0.516	
11	H6	0.246		37	H19	0.451	
12	H6′	0.236		38	C20	-0.052	
13	C7	-0.232		39	H20	0.243	
14	H7	0.220		40	C21	-0.059	
15	C8	-0.335		41	H21	0.232	
16	H8	0.199		42	N22	-0.574	Ring3 Charge= (-1.215)+ (1.420)=0.205
17	H8′	0.207		43	C23	0.270	
18	O9	-0.460	Charge= (-1.002)+ (0.916)= -0.086	44	H23	0.229	
19	H2	0.513		45	N24	-0.521	
20	O10	-0.542		46	H24	0.449	
21	H3	0.403		47	C25	-0.055	
23	Fe11	0.995	0.995	48	H25	0.242	
24	N12	-0.563		49	C26	-0.065	
25	C13	0.262		50	H26	0.230	
26	H13	0.233		Net Charge=2.001			

[a]Optimized structure of TS2 and some important bond lengths (Å) and total net charges at the different components of TS2 are shown in Figure 3 (b).

Table S7. NBO charges at different atoms of product complex PC2 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C2 and C3 sites of allicin in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.406	Allicin	27	N14	-0.518	Ring1 Charge= (-1.239)+ (1.437)=0.198
2	H1	0.247		28	H14	0.451	
3	H1′	0.243		29	C15	-0.055	
4	C2	0.081		30	H15	0.244	
5	C3	-0.518		31	C16	-0.062	
6	H3′	0.265	Charge= (-3.052)+ (3.161) =0.109	32	H16	0.233	
7	S4	1.187		33	N17	-0.595	Ring2 Charge= (-1.218)+ (1.427)=0.209
8	O4	-0.938		34	C18	0.262	
9	S5	-0.020		35	H18	0.235	
10	C6	-0.576		36	N19	-0.514	
11	H6	0.276		37	H19	0.452	
12	H6′	0.244		38	C20	-0.051	
13	C7	-0.213		39	H20	0.244	
14	H7	0.211		40	C21	-0.058	
15	C8	-0.383		41	H21	0.234	
16	H8	0.211		42	N22	-0.607	Ring3 Charge= (-1.228)+ (1.423)=0.195
17	H8′	0.196		43	C23	0.244	
18	O9	-0.427	Charge= (-0.939)+ (0.993)= 0.054	44	H23	0.242	
19	H2	0.490		45	N24	-0.519	
20	O10	-0.512		46	H24	0.453	
21	H3	0.503		47	C25	-0.044	
23	Fe11	1.238	1.238	48	H25	0.248	
24	N12	-0.604		49	C26	-0.058	
25	C13	0.273		50	H26	0.236	
26	H13	0.236		Net Charge=2.003			

[a]Optimized geometry of PC2 and some important bond lengths (Å) and total net charges at the different components of PC2 are shown in Figure S1 (b).

Table S8. NBO charges at different atoms of TS3 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C6 and C7 sites of allicin forming product complex PC3 in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.317	Allicin	27	N14	-0.518	Ring1 Charge= (-1.199)+ (1.403)=0.204
2	H1	0.209		28	H14	0.450	
3	H1′	0.199		29	C15	-0.050	
4	C2	-0.250		30	H15	0.243	
5	H2	0.224		31	C16	-0.066	
6	C3	-0.581	Charge= (-2.905)+ (3.301) =0.396	32	H16	0.230	
7	H3	0.264		33	N17	-0.565	Ring2 Charge= (-1.190)+ (1.415)=0.225
8	H3′	0.258		34	C18	0.258	
9	S4	1.166		35	H18	0.233	
10	O4	-0.973		36	N19	-0.517	
11	S5	0.282		37	H19	0.451	
12	C6	-0.208		38	C20	-0.053	
13	H6′	0.263		39	H20	0.243	
14	C7	-0.336		40	C21	-0.055	
15	C8	-0.240		41	H21	0.230	
16	H8	0.218		42	N22	-0.565	Ring3 Charge= (-1.205)+ (1.417)=0.212
17	H8′	0.218		43	C23	0.265	
18	O9	-0.462	Charge= (-0.975)+ (0.931)= -0.044	44	H23	0.230	
19	H6	0.514		45	N24	-0.520	
20	O10	-0.513		46	H24	0.450	
21	H7	0.417		47	C25	-0.053	
23	Fe11	1.006	1.006	48	H25	0.242	
24	N12	-0.565		49	C26	-0.067	
25	C13	0.244		50	H26	0.230	
26	H13	0.236		Net Charge=1.999			

[a]Optimized geometry of TS3 and some important bond lengths (Å) and total net charges at the different components of TS3 are shown in Figure 4 (a).

Table S9. NBO charges at different atoms of product complex PC3 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C6 and C7 sites of allicin in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.327	Allicin	27	N14	-0.529	Ring1 Charge= (-1.264)+ (1.432=0.168
2	H1	0.206		28	H14	0.479	
3	H1′	0.197		29	C15	-0.047	
4	C2	-0.244		30	H15	0.242	
5	H2	0.220	Charge=	31	C16	-0.067	
6	C3	-0.578	(-3.066)+	32	H16	0.234	
7	H3	0.254	(3.124)	33	N17	-0.594	Ring2 Charge= (-1.218)+ (1.429)=0.211
8	H3′	0.243	=0.058	34	C18	0.264	
9	S4	1.125		35	H18	0.235	
10	O4	-0.999		36	N19	-0.514	
11	S5	0.092		37	H19	0.452	
12	C6	-0.446		38	C20	-0.052	
13	H6′	0.266		39	H20	0.244	
14	C7	0.034		40	C21	-0.058	
15	C8	-0.472		41	H21	0.234	
16	H8	0.245		42	N22	-0.606	Ring3 Charge= (-1.241)+ (1.438)=0.197
17	H8′	0.242		43	C23	0.272	
18	O9	-0.478	Charge=	44	H23	0.238	
19	H6	0.532	(-0.899)+	45	N24	-0.518	
20	O10	-0.421	(1.025)=	46	H24	0.451	
21	H7	0.493	0.126	47	C25	-0.054	
23	Fe11	1.241	1.241	48	H25	0.244	
24	N12	-0.621		49	C26	-0.063	
25	C13	0.244		50	H26	0.233	
26	H13	0.233		Net Charge=2.001			

[a]Optimized geometry of PC3 including some important bond lengths (Å) and total net charges at the different components of PC3 are shown in Figure S2 (a).

Table S10. NBO charges at different atoms of TS4 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C7 and C8 sites of allicin forming product complex PC4 in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.314	Allicin	27	N14	-0.514	Ring1 Charge= (-1.191)+ (1.422)=0.231
2	H1	0.208		28	H14	0.452	
3	H1′	0.200		29	C15	-0.048	
4	C2	-0.243		30	H15	0.244	
5	H2	0.216		31	C16	-0.063	
6	C3	-0.568	Charge= (-3.015)+ (3.209) =0.194	32	H16	0.234	
7	H3	0.258		33	N17	-0.571	Ring2 Charge= (-1.203)+ (1.427)=0.224
8	H3′	0.251		34	C18	0.267	
9	S4	1.125		35	H18	0.235	
10	O4	-0.954		36	N19	-0.518	
11	S5	0.116		37	H19	0.450	
12	C6	-0.541		38	C20	-0.051	
13	H6	0.277		39	H20	0.243	
14	H6′	0.267		40	C21	-0.063	
15	C7	-0.159		41	H21	0.232	
16	C8	-0.236		42	N22	-0.580	Ring3 Charge= (-1.204)+ (1.419)=0.215
17	H8′	0.291		43	C23	0.259	
18	O9	-0.238	Charge= (-0.420)+ (0.591)= 0.171	44	H23	0.231	
19	H7	0.295		45	N24	-0.513	
20	O10	-0.182		46	H24	0.453	
21	H8	0.296		47	C25	-0.040	
23	Fe11	0.967	0.967	48	H25	0.246	
24	N12	-0.566		49	C26	-0.071	
25	C13	0.257		50	H26	0.230	
26	H13	0.235		Net Charge=2.002			

[a]Optimized geometry of TS4 and some important bond lengths (Å) and total net charges at the different components of TS4 are shown in Figure 4 (b).

Table S11. NBO charges at different atoms of product complex PC4 in presence of Fe-SOD involving double hydrogen atom transfer to superoxide radical anion from the C7 and C8 sites of allicin in aqueous media obtained at M06-2X/6-311+G(d) level of theory.[a]

Sl. No.	Atoms	NBO Charge	Total	S. No.	Atoms	NBO Charge	Total
1	C1	-0.311	Allicin	27	N14	-0.515	Ring1 Charge= (-1.197)+ (1.425)=0.228
2	H1	0.208		28	H14	0.452	
3	H1′	0.200		29	C15	-0.048	
4	C2	-0.250		30	H15	0.244	
5	H2	0.215		31	C16	-0.064	
6	C3	-0.570	Charge= (-2.918)+ (3.156) =0.238	32	H16	0.234	
7	H3	0.259		33	N17	-0.563	Ring2 Charge= (-1.197)+ (1.418)=0.221
8	H3′	0.256		34	C18	0.263	
9	S4	1.127		35	H18	0.234	
10	O4	-0.942		36	N19	-0.519	
11	S5	0.088		37	H19	0.449	
12	C6	-0.577		38	C20	-0.053	
13	H6	0.280		39	H20	0.242	
14	H6′	0.270		40	C21	-0.062	
15	C7	-0.082		41	H21	0.230	
16	C8	-0.186		42	N22	-0.589	Ring3 Charge= (-1.222)+ (1.431)=0.209
17	H8′	0.253		43	C23	0.258	
18	O9	-0.443	Charge= (-0.860)+ (1.019)= 0.159	44	H23	0.240	
19	H7	0.518		45	N24	-0.513	
20	O10	-0.417		46	H24	0.453	
21	H8	0.501		47	C25	-0.043	
23	Fe11	0.941	0.941	48	H25	0.246	
24	N12	-0.570		49	C26	-0.077	
25	C13	0.258		50	H26	0.234	
26	H13	0.237		Net Charge=1.996			

[a]Optimized structure of PC4 and some important bond lengths (Å) and total net charges at the different components of PC4 are shown in Figure S2 (b).

Table S12. Imaginary frequencies (cm^{-1}) and tunneling coefficients Γ(T) for double hydrogen atom transfer to super oxide radical anion in absence and presence of Fe-SOD from the different pairs of sites ((C1,C2), (C2,C3), (C6,C7) and (C7,C8)) of allicin in gas phase obtained at M06-2X/6-311+G(d) level of theory.

S. No.	Reaction Site	Absence of Fe-SOD[a]		Presence of Fe-SOD[a]	
		Freq.	Γ(T)	Freq.	Γ(T)
1	(C1,C2)	i1273.44	27.03 (29.11)	i997.00	0.32 (3.15)
2	(C2,C3)	i1943.78	681.86 (3801.27)	i353.44	0.76 (1.13)
3	(C6,C7)	i968.75	0.34 (3.18)	i1132.78	0.20 (2.0)
4	(C7,C8)	i1050.38	4.31 (4.30)	i1350.44	0.0 (20.61)

[a]Values given in parentheses were obtained in aqueous media.

Table S13. Imaginary frequencies (cm^{-1}) and tunneling coefficients Γ(T) for hydrogen atom transfer to $OH^{\cdot}$, $NO_2^{\cdot}$ and $OCH_3^{\cdot}$ from the different sites (C1-C8) of allicin in gas phase obtained at M06-2X/6-311+G(d) level of theory.

S. No.	Reaction Site	$OH^{\cdot}$		$NO_2^{\cdot}$		$OCH_3^{\cdot}$	
		Freq.	Γ(T)[a]	Freq.	Γ(T)[a]	Freq.	Γ(T)[a]
1	C1	i1598.10	539.33 (569.92)	i1586.41	20.45 (19.62)	i1647.75	90.23 (80.00)
2	C2	i1470.66	91.08 (127.04)	i1573.98	15.07 (13.31)	i1679.74	505.47 (450.10)
3	C3	i1414.35	30.80 (42.64)	i1876.76	3110.16 (3047.43)	i1815.24	253.13 (166.32)
4	C6	i1061.12	4.40 (4.45)	i1821.45	703.49 (759.06)	i1683.08	468.86 (336.309)
5	C7	i1628.32	141.54 (174.74)	i1627.34	54.37 (64.07)	i1646.31	149.61 (237.56)
6	C8	i1565.84	351.84 (439.66)	i1652.04	21.42 (16.38)	i1608.94	52.90 (68.54)

[a]Values given in parentheses were obtained in aqueous media.