On the mechanism of the synergistic oxidation of saturated hydrocarbons and hydrogen sulfide under Gif conditions

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It is demonstrated by a study of cyclohexane phenylselenation that the synergistic oxidation of cyclohexane with H_2S and O_2 does not involve carbon or oxygen radicals.

Recently we reported a new reaction in which saturated hydrocarbons were oxidized synergistically with H_2S and O_2.[1] This unusual reaction is an extension of Gif chemistry that should be of industrial importance. We now present further evidence on the mechanism of this reaction.

The bond strength[2] in the H–SH bond is 90.5 (±1.1) kcal mol^{-1}. Thus any secondary or primary carbon radical would be immediately reduced by H-atom transfer. When we photolyzed the Barton ester of adamantane-1-carboxylic acid in the presence of H_2S it was converted quantitatively into adamantane. Similarly, oxidation of adamantane in the presence of H_2S gave a *normalized* secondary/tertiary ratio of about 1. This is three times as great as normal and corresponds to the reduction of tertiary radicals back to hydrocarbon.[3] Since there are no secondary radicals, secondary position oxidation proceeded normally.

Cyclohexane gave a mixture of cyclohexanone and cyclohexanol. The latter was produced by reduction of the intermediary hydroperoxide[4] by H_2S.

The formation of alcohol and ketone at the same time enabled us to determine the kinetic isotope effect (KIE) for alcohol formation. It was of the order 1.1–1.2.

Recently[5] we showed that phenylselenation of saturated hydrocarbons[6a] involves PhSeH, an excellent trap for radicals.[6b] In fact the earlier work[6a] involved reduction with Zn^0–Fe^{II} catalyst. Methylation showed that all the PhSeSePh had been reduced to PhSeH.[7] This was, in fact, a proof of the non-involvement of carbon radicals. Our recent work[5] has shown that selenide anion is not involved.[8] Another factor to consider is the relative rates of reaction (3×10^9 and 2.3×10^7 M^{-1} s^{-1}) for radicals with PhSeH and PhSeSePh, respectively.[6b]

In the present study, PhSeSePh was added to a system where H_2S and O_2 were being passed through a mixture of cyclohexane and picolinic acid (Table 1). This afforded ketone, alcohol and a very high yield of phenylselenocyclohexane with respect to the amount of PhSeSePh added (entries 1 and 2). Unlike in the earlier study[5] using H_2O_2, when H_2S was used the picolinic acid was no longer needed. The phenylselenocyclohexane was then produced in quantitative yield (entries 3, 4 and 5).

We consider that phenyselenocyclohexane must be produced by the same type of mechanism that we proposed before[5] (Scheme 1).

In our first publication on the H_2S–O_2 reaction[1] we did not comment on the mechanism except to classify it as 'Gif chemistry'. We suggested that the oxidant was superoxide and that this reacted with Fe^{II} to furnish the species Fe^{III}–OOH. The species can also be produced by displacement on Fe^{III} with H_2O_2. Without hydrocarbon this has $t_{\frac{1}{2}}$ *ca.* 45 min. Upon addition of hydrocarbon it is rapidly inserted into the Fe–C bond, which slowly ($t_{\frac{1}{2}}$ *ca.* 45 min) affords ketone or, with iodide, rapidly gives the iodide of the hydrocarbon.[9] In order to explain why the selective functionalization of saturated hydrocarbons takes place in the presence of H_2S, Ph_2S, Ph_3P, $(MeO)_3P$, PhSH and even PhSeH, we proposed in 1992 that it was the contact of a relatively inert iron species with the hydrocarbon which created the active iron species, which then reacted immediately with the hydrocarbon. We cited the agostic effect[10] as an explanation. It is the reactivity of PhSeH, produced by[5] PhSeSePh and Bu_3P, that gives real substance to our proposal. We now suggest that Fe^{IV} and Fe^{V} are only produced at the moment of contact with the hydrocarbon and that these species react instantly with their hydrocarbon activator. We offer the same explanation for the KIE of close to 1 (see above).

Thus the Fe^{III}–Fe^{V} manifold can be modified according to Scheme 2. The H_2S–O_2 chemistry then takes place by H_2S reduction of Fe^{V} to Fe^{IV}.

The alternative route for phenylselenation is from Fe^{II} and H_2O_2, which we have used in our work with PhSeSePh and Bu_3P already cited. We modify our concept of the Fe^{II}–Fe^{IV} manifold as shown in Scheme 3. Normally, the Fe^{IV}–CHR_2 species can fragment into Fe^{III} and a carbon radical. This, however, does not happen when $PhSe^-$ is one of the ligands.

In our recent work on the phenylselenation reaction we showed by ^{77}Se NMR spectroscopy that the reaction of PhSeSePh and Bu_3P (50% excess) with a drop of water was an excellent method for quantitative synthesis of PhSeH *in situ*. The presence of the excess Bu_3P guaranteed that there was no

Table 1 Effect of selenide on Gif oxidation[a]

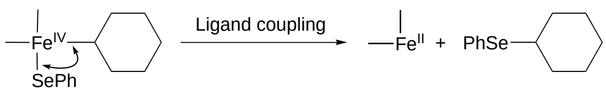
Entry	Ligand (mmol)	Selenide (mmol)	$FeCl_2\cdot4H_2O$/ (mmol)	Cyclohexane/ (mmol)	Ketone/ (mmol)	Alcohol/ (mmol)	$PhSeC_6H_{11}$/ (mmol)	Conversion[b] (%)	Yield[c] (%)
1	Picolinic acid (3)	PhSeSePh (1)	1	20	0.75	2.31	1.81	24.35	90.5
2	Picolinic acid (3)	PhSeH (1.5)	1	20	0.15	0.51	1.46	10.6	97.3
3	—	PhSeH (2.5)	1	20	0.74	1.32	2.51	22.85	100
4	—	PhSeSePh (1.5)	1	20	1.28	2.50	3.03	30.85	100
5	—	PhSeSePh (1)	1	20	1.00	2.19	1.98	25.85	99
6	—	PhSeSePh (1)	1	5	0.19	0.40	0.95	30.8	47.5
7	—	PhSeSePh (1)	1	2	0.10	0.15	0.75	50	37.5

[a] Ligand (0–3 mmol), $FeCl_2\cdot4H_2O$ (0.3–1 mmol), cyclohexane (2–20 mmol), selenide (1–2.5 mmol), 4-*tert*-butylpyridine (2 ml), MeCN (31 ml). O_2 (g) and H_2S (g) were passed at atmospheric pressure through the reaction mixture at room temperature for 3–4 h. The products were analyzed by GC, naphthalene was used as internal standard. [b] Conversion based on cyclohexane. [c] Yield based on selenide.

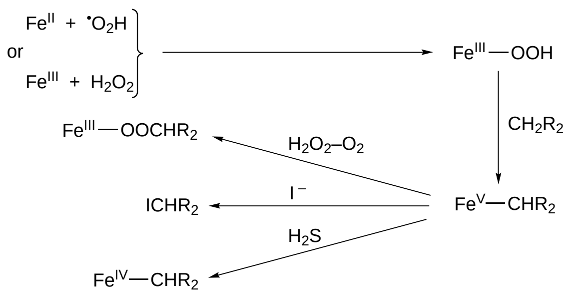
Table 2 Phenyselenation in the presence of Bu_3P[a]

Entry	PhSePh/ mmol	Bu_3P/ mmol	LiCl/ mmol	Conditions	Chloride/ mmol	Ketone/ mmol	Alcohol/ mmol	$PhSeC_6H_{11}$/ mmol
1[b]	1	8	—	$H_2S–O_2$	—	0.73	1.98	1.85
2[b]	2	60	—	$H_2S–O_2$	—	0.39	1.07	0.83
3[c]	2	3	—	$H_2S–H_2O_2$ (1)	—	—	—	0.74
4[c]	2	3	—	$H_2S–H_2O_2$ (2)	—	—	—	1.30
5[c]	4	6	—	$H_2S–H_2O_2$ (1)	—	—	—	0.85
6[c]	4	6	—	$H_2S–H_2O_2$ (2)	—	—	—	1.54
7[c]	4	6	—	$H_2S–H_2O_2$ (3)	—	—	—	1.92
8[c]	4	6	—	$H_2S–H_2O_2$ (4)	—	—	—	2.55
9[d]	1	2	20	H_2O_2 (1)	0.23	—	—	0.69
10[d]	1	2	20	H_2O_2 (2)	0.34	—	—	1.05

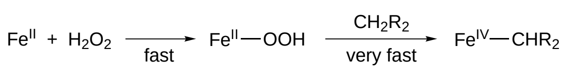
[a] Picoline acid (3 mmol), $FeCl_2 \cdot 4H_2O$ (1 mmol), cyclohexane (20 mmol), PhSeH (0.5–4 mmol), 4-*tert*-butylpyridine (2 ml), MeCN (31 ml). The products were analyzed by GC, naphthalene was used as internal standard. [b] O_2 (g) and H_2O (g) were passed through the reaction mixture at room temperature for 3–4 h. [c] H_2S (g) was passed through the reaction mixture at 0 °C when H_2O_2 (1–4 mmol) was added. [d] H_2O_2 (1–2 mmol) was added at 0 °C.



Scheme 1



Scheme 2



Scheme 3

adventitious oxidation of PhSeH back to PhSeSePh. We studied this reaction by ^{31}P NMR spectroscopy and showed that the reduction was complete in 2 min (experiment by Dr J. A. Smith). Before adding H_2O_2 we waited for 10–20 min to make sure that the reduction was complete.

Table 2 shows further experiments in which Bu_3P is used in the presence of PhSeSePh. Entries 1 and 2 used the $H_2S–O_2$ system as studied in Table 1. For entry 1 the yield of phenylselenocyclohexane was 92%, whilst the total activation including ketone and alcohol was 4.56 mmol. This is a good conversion as judged by past experiments.[1] All the selenium was present as PhSeH prior to reaction with the hydrocarbon yet the ketone and alcohol were formed in significant amounts. So not only are no radicals present but also the Bu_3P does not react with the iron species prior to activation by the hydrocarbon.

Using H_2O_2 as a minor component in the presence of an excess of PhSeH, the yield of the phenylselenocyclohexane (the only product) was 74 and 85% for entries 3 and 5, respectively (for 1 mmol of H_2O_2), and 65 and 77% for entries 4 and 6, respectively (for 2 mmol of H_2O_2). The increased yields in entries 5 and 6 were due to an increase in the available PhSeH. A further increase in the amount of H_2O_2 (entries 7 and 8) reduced the yield with respect to H_2O_2 to 64%.

The formation of cyclohexyl chloride in the Fe^{II}–Fe^{IV} manifold is usually accepted[11] to imply the reaction of a carbon radical with an Fe^{III}–Cl bond. The reaction can also be considered as a ligand-coupling reaction with an Fe^{IV}–C bond as in formation of the selenide (Scheme 1). The formation of cyclohexyl chloride using H_2O_2, like the phenylselenation reaction, requires the presence of the right carboxylic acid (here picolinic acid) and the correct amount of a suitable pyridine base (here 4-*tert*-butylpyridine). If the formation of the chloride can only take place *via* radical formation then the presence of PhSeH would remove the radical and no chloride would be formed. In fact entries 9 and 10 show that chloride formation is in competition with the phenylselenation reaction.

Finally we examined an oxidant, *tert*-butyl hydroperoxide (TBHP), that always reacts with Fe^{II} to make *tert*-butoxy radicals.[12–14] When TBHP (3 mmol) was added to cyclohexane (20 mmol) in MeCN (31 ml) and 4-*tert*-butylpyridine (2 ml) containing $FeCl_2 \cdot 4H_2O$ (1 mmol) and picolinic acid (3 mmol) with passage of H_2S, only traces of oxidation (0.05 mmol) were seen. From workup, 3 mmol of *tert*-butyl alcohol were recovered. This result is in keeping with the reduction of *tert*-butoxy radicals by H_2S. We conclude that carbon and oxygen radicals do not play a role in the synergistic oxidation of saturated hydrocarbons.

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Notes and References

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