

[FeS/FeS₂]. A REDOX SYSTEM FOR THE ORIGIN OF LIFE

(some experiments on the Pyrite-Hypothesis)

MICHAEL KASCHKE, MICHAEL J. RUSSELL

Department of Geology and Applied Geology, University of Glasgow, Glasgow G12 8QQ, Scotland

and

W. JOHN COLE

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

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Abstract. The FeS/FeS₂ redox system, whose importance is stressed in recent theories on the origin of life, has been tested experimentally. In this paper it is demonstrated by thermodynamical calculations as well as by experiments, that cyclohexanone, which served as model compound, can be reduced by the aforementioned redox system. Reactions were carried out in methanol and DMF at 25 °C and at 100 °C. Besides products that were synthesised in both solvents, like cyclohexanethiol and dicyclohexyldisulphide, special compounds were obtained in methanol and in DMF, because of the involvement of the respective solvent in the reaction. Yields of reduced compounds were lower in methanol owing to a compound that hindered the reduction (cyclohexylketal). With increasing temperature and duration the amount of reduced compounds increased. Further experiments have shown that 1,1-cyclohexanedithiol is likely to be a necessary intermediate for the reduced products. The experiments give evidence to the 'pyrite hypothesis', which postulates that the FeS/FeS₂ redox system was of importance for the origin of life.

1. Introduction

Recent theories stress the importance of iron and sulphur for life's beginnings. A sophisticated theory introduced by Wächtershäuser (1988a, b, c) is based on the formation of pyrite (FeS₂) from iron monosulphide (FeS) and hydrogen sulphide (H₂S). Due to the low redox potential of this FeS/FeS₂ redox system, simple molecules e.g. formaldehyde (HCHO) could have been reduced to more complex organic molecules. As organic molecules containing more than one negative charge are electrostatically attracted by the surface of iron monosulphide or pyrite, the first metabolism could have taken place on the surface of iron sulphide minerals as two dimensional systems (Wächtershäuser, 1988b, c).

Another approach introduced by Russell *et al.* (1988, 1989) and Russell and Daniel (1992) attaches more importance to the geological aspects of the environment where the origin of life could have taken place, i.e. the initial conditions. They argue that medium temperature (200 °C) high pressure (300 bar) hot springs on the deep ocean floor away from spreading centres, were the likely site of life's origins. Here, over 4 billion years ago colloidal iron sulphide membranes are assumed to have formed as bubbles at the interface between off-axis alkaline spring waters and the mildly acid ocean. It is such botryoids that are assumed to have been the reproducing

culture and catalytic chambers or protocells which prevented the immediate dissipation of molecules with high chemical energy into the relatively oxidized oceans (Cairns-Smith *et al.*, 1992). That the off-axis hot springs were alkaline is a result of dissolution of calcium from the Mg, Fe, Ca silicates of the Hadean ocean crust, just as today groundwater springs in ophiolites (ocean crust thrust on to the continents) generally has a pH of ~ 12 (Barnes and O'Neil, 1969; Neal and Stanger, 1984). In contrast the oceans were probably mildly acidic (pH ~ 6.5) because of the likely very high atmospheric pressure where $p\text{CO}_2$ was ~ 50 bars (Walker, 1986; Kasting and Ackerman, 1986).

The inspiration for this idea lies in the discovery of such 'fossilized' bubbles (botryoids and fine chimneys ~ 1 mm in diameter at the 350 million year old Silvermines deposit in Ireland (Larter *et al.*, 1981). In this case the ocean was mildly alkaline, as it is today and the hydrothermal solutions acid as a result of the precipitation of magnesium ions as the hydroxide brucite within a more siliceous crust (Russell, 1983). We have grown fine iron sulphide chimneys and bubbles in the laboratory by passing sodium sulphide solution through a 0.5 mm aperture at the base of a flask containing ferrous chloride solution (the Hadean analogue). The same forms are produced if the fluids are reversed (the 350 My old example) (Russell *et al.*, 1989; Cairns-Smith *et al.*, 1992).

Both the Wächtershäuser and the Russell approaches require H_2S , Fe(II) and other simple molecules such as HCHO. Here we report some experiments related to the FeS/FeS₂ redox system proposed by Wächtershäuser (1988a, b, c).

Cyclohexanone was used as model compound for carbonyl groups for these experiments. Cyclohexanone is advantageous in that it, and the resulting products, are easily analysed by gas chromatography-mass spectrometry (GC-MS), our main analytical method. Methanol and dimethylformamide (DMF) were used as solvents. Our justification for the use of organic solvents is that under the predicted conditions of the origin of life at high temperature and high pressure (around 200 °C and 300 bar), the characteristics of water approach those of organic solvents. Siskin and Katritzky (1991) have shown experimentally that under such conditions organic reactions like condensations can be carried out in water. They are no longer restricted to organic solvents, for example, at 250 °C and 40 bar, aldol condensation of 1-decanal has been observed (Siskin and Katritzky, 1991). Determination of the dielectrical constant ϵ shows that its value for water (78.54, NTP, Weast, 1984) decreases with increasing pressure and temperature to approximate values typical of organic solvents (DMF: 36.7, NTP, Dupont Durst and Gokel, 1987; methanol: 32.63, NTP, Weast, 1984, acetone: 20.7, NTP, Weast, 1984). At 200 °C and 300 bar the dielectrical constant of water is 35.91 (Weast, 1984). As a consequence of these experiments we argue that origin of life type reactions in organic solvents might approximate the conditions on the early Earth without necessarily resorting to high pressure and high temperature aqueous reactions.

Our procedural method is to consider the redox system as a black box, and to concentrate on the products resulting from the treatment of the initial compound

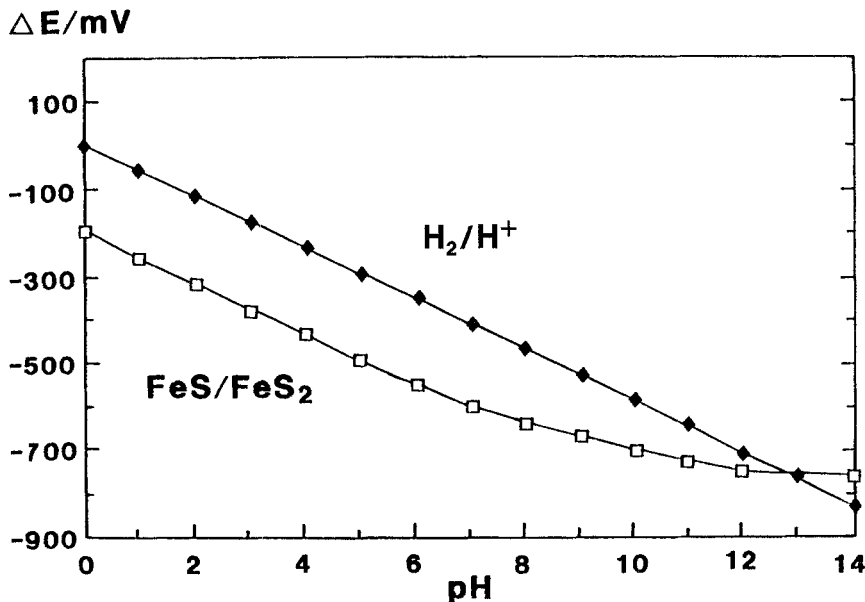
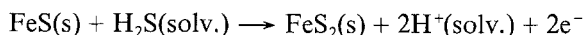


Fig. 1. Plot of the redox potential (ΔE) of the authentic FeS/FeS₂ redox system as function of pH. Calculations are performed for aqueous solution with the Nernst equation at 25 °C. The function for the H₂/H⁺ redox system is given as an example for linear pH dependence. These thermodynamical calculations assume that (i) $a(\text{FeS}) = a(\text{FeS}_2) = a(\text{H}_2\text{S}) + a(\text{SH}^-) + a(\text{S}^{2-}) = 1 \text{ mol L}^{-1}$ and (ii) $a(\text{H}_2) = 1 \text{ mol L}^{-1}$

cyclohexanone with the redox system. The products can be divided into two groups, those that can be explained by condensation reactions, and those reduced compounds whose synthesis is presumed to be due to the 'FeS/FeS₂' redox system. We write the redox system in brackets ([FeS/FeS₂]) when we talk about it as a black box in order to indicate its symbolical character. We note that even pyrite itself is not necessarily produced.

FeS/FeS₂-system

This redox system can be represented by the following equation:



Here $\Delta G(\text{FeS/FeS}_2, \text{std})$ is $-38.6 \text{ kJ mol}^{-1}$ [$\Delta G_f^\circ(\text{FeS}) = -100.42 \text{ kJ mol}^{-1}$ (Weast, p. D-71); $\Delta G_f^\circ(\text{FeS}_2) = -167 \text{ kJ mol}^{-1}$ (Weast, p. D-71) and $\Delta G_f^\circ(\text{H}_2\text{Saq}) = -27.87 \text{ kJ mol}^{-1}$ (Bard *et al.*, p. 97)]. The respective redox potential is -200 mV . The pH dependence is illustrated in Figure 1. The more elevated the pH, the stronger the redox capacity should be from thermodynamical considerations. Unlike the H₂/H⁺ system, the presented system shows linear behaviour only from pH 0 to 7. At higher pH values the dissociation of hydrogen sulphide causes non-linear behaviour ($\text{pKs}(1)=7$, $\text{pKs}(2)=12$).

The FeS/FeS₂ system has been tested by Drobner *et al.* (1990) in an aqueous H₂S solution at pH=6.5 in oxygen free sealed bottles at 100 °C. Within 14 days about 1% of H₂S reacted with iron sulphide to yield pyrite. This means that this reaction is from the chemical viewpoint a slow one (but perhaps fast by geological standards). Similar observations have been made by Taylor *et al.* (1979).

We intend to reduce the carbonyl group of cyclohexanone with the [FeS/FeS₂] redox system. One possible reaction where the carbonyl group is reduced is illustrated in the following equation:



Here $\Delta G(\text{carb./thiol, std.}) = 10 \text{ kJ mol}^{-1}$; $R_2 = (\text{CH}_2)_5$

Experimental Procedures

All experiments were carried out with cyclohexanone as the model compound. Cyclohexanone (AnalaR, BDH) was used without further purification. Methanol was distilled with a vigreux column and dried overnight with anhydrous MgSO₄. DMF (GPR, BDH) was distilled under reduced pressure and dried over anhydrous MgSO₄. The H₂S was either taken from a gas cylinder (BDH) or synthesized *in situ* from Na₂S · 9H₂O and HAc or Na₂S · 9H₂O and NH₄Cl. Glacial acetic acid (GPR, BDH) was purified by refluxing it for 5 hr with 5% KMnO₄ in order to oxidise acetaldehyde and other organic compounds. After distillation HAc was dried with anhydrous MgSO₄ overnight. Ammonia was synthesized using NH₄Cl (GPR, BDH) and NaOH (GPR, BDH). FeCl₂ · 4H₂O (GPR, Fisons) was dissolved and treated with elemental zinc at 60 °C under nitrogen in order to remove Fe(III).

The petroleum ether (b.p. 40–60 °C) used for extraction of organic compounds was purified by shaking twice with concentrated sulphuric acid and then with a 10% solution of the acid. Finally it was shaken with concentrated KMnO₄ until the colour persisted, washed with water, distilled and dried over anhydrous CaCl₂.

Generally there were three different experimental procedures. One was based on the use of excess of gaseous hydrogen sulphide bubbled into the reaction vessel (procedure A) and the next was related to the synthesis of hydrogen sulphide stoichiometrically *in situ* in the sealed reaction vessel (procedure B). Both procedures were carried out with and without FeCl₂ · 4H₂O. Procedure C was also carried out in sealed bottles. This time, the starting material was 1,1-cyclohexane-dithiol.

Procedure A

Cyclohexanone (15 mmol), FeCl₂ · 4H₂O (5 mmol) and NH₃ (5 mmol) were dissolved in DMF (80 ml) in a two necked reaction flask (250 ml). One neck was used for a sintered glass bubbler for input of the hydrogen sulphide (flow rate: 1 mol h⁻¹). The other neck contained a condenser connected to a burette serving as a bubble

flow meter. H₂S was bubbled in for 4-hr at room temperature. The calculated initial pH for aqueous solution is 11.

Procedure B

The reactions were carried out in a teflon cap sealed rota flow vessel (50 ml) which was initially filled with nitrogen. The vessel contained cyclohexanone and FeCl₂ · 4H₂O (2 mmol) dissolved in 25 ml of the corresponding solvent (DMF or methanol). 8 mmol of H₂S (SH⁻ at the existing pH) were synthesized *in situ* from Na₂S · 9H₂O and NH₄Cl or HAc. In reactions R2(Fe), R3(Fe) and R4(Fe) (Table II), NH₄Cl was used. Here the necessary base is produced at the same time. In reaction R5(Fe) HAc was chosen and the base (dimethylamine) was synthesised *in situ* by the decomposition of DMF. The reaction times varied from 4 to 16 days and were carried out at 25 and 100 °C. The calculated initial aqueous pH for the reactions where Na₂S · 9H₂O/HAc is used (R2(Fe), R3(Fe), R4(Fe)) is 8.4 whereas the value for R5(Fe), which contains Na₂S · 9H₂O/NH₄Cl, is 10.6.

Procedure C

The distilled geminal cyclohexanedithiol (10 mmol, synthesized in R1(Fe)) was taken as initial compound and treated at 100 °C with (i) Na₂S · 9H₂O (10 mmol) in methanol/DMF (25 ml, 2:1), R6 (ii) methanol/DMF (25 ml, 1:2) only, R7 and (iii) Na₂S · 9H₂O in methanol (25 ml), R8.

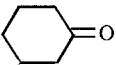

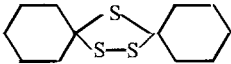
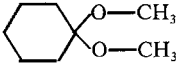
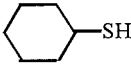
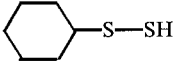
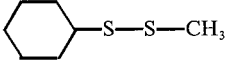
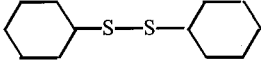
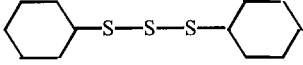
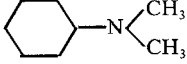
Extraction procedure (same for A, B and C)

At the completion of the reaction the mixture was filtered, any iron sulphide present washed with oxygen-free water (milli QTM grade) and acetone, then dried over silica gel and analysed by X-ray diffraction. The filtrate was neutralised with HCl and twice extracted with 50 ml of petroleum ether (b.p. 40–60 °C). The extracts were combined, washed with water (milli QTM grade) and dried over anhydrous MgSO₄. The petroleum ether was then distilled and the remaining liquid analysed by GC and GC-MS.

Analysis by Gas Chromatography

Gas chromatographic separations were achieved with an Hewlett-Packard 5880A instrument equipped with a CP Sil 5 CB (Chrompack) fused silica capillary column (25 m × 0.32 mm I.D. × 0.12 μm) and a flame ionisation detector (FID). The Grob-type injector was operated in split mode (50:1) and the helium carrier- and make-up gas flow rate were 2 and 25 ml min⁻¹ respectively. The column temperature was programmed from 50 °C (2 min) to 275 °C (5 min) at 5 °C min⁻¹. The injection port and detector temperatures were 255 and 260 °C respectively.

TABLE I
Detected products with corresponding retention times and principal MS ions

Formula	$t_r(\text{rel.})^a$	Principal ions (m/z) with relative abundances in parentheses
	1.00	98(30), 83(10), 69(26), 55(100), 42(85), 27(34)
(P1) 	1.71 and 1.79 ^b	114(25), 99(8), 85(10), 81(100), 79(30), 71(30), 58(12), 45(20)
(P2) 	11.13	260(40), 195(15), 146(16), 115(45), 81(100), 71(16)
(P3) 	2.11	144(12), 113(50), 101(100), 81(30), 55(20)
(P4) 	1.43	116(70), 83(60), 82(80), 73(15), 67(100), 60(14), 55(90), 45(50) 41(70)
(P5) 	3.45	148(5), 115(40), 114(10), 99(4), 85(5), 81(100), 71(20), 58(20) 45(15)
(P6) 	4.94	162(40), 83(28), 80(50), 79(24), 55(100), 45(25)
(P7) 	10.00	230(25), 148(45), 83(100), 55(80), 41(45)
(P8) 	11.85	262(80), 180(20), 115(40), 83(100), 55(80), 41(60)
(P9) 	1.87	127(20), 98(5), 84(100), 71(25), 42(18)

^a $t_r(\text{rel.}) = \frac{t_r(\text{TIC}) \text{ of compound}}{t_r(\text{TIC}) \text{ of Cyclohexanone (2.57 min } \pm 0.1)} \pm 0.05$.

^b Hydrogen sulphide abstracted on volatilisation in injection port. Retention times are due to the resulting thione and enthiol.

Analysis by Gas Chromatography-Mass Spectrometry

Analyses were carried out with an Hewlett-Packard 5971 mass selective detector interfaced to a 5890 series II gas chromatograph and computer (Vectra QS/165). Separations were effected with HP1 fused silica column (12.5 m \times 0.2 mm I.D. \times 0.33 μm). Injection and temperature programming conditions were identical to those for GC above. Retention times from the total ion current (TIC) traces prac-

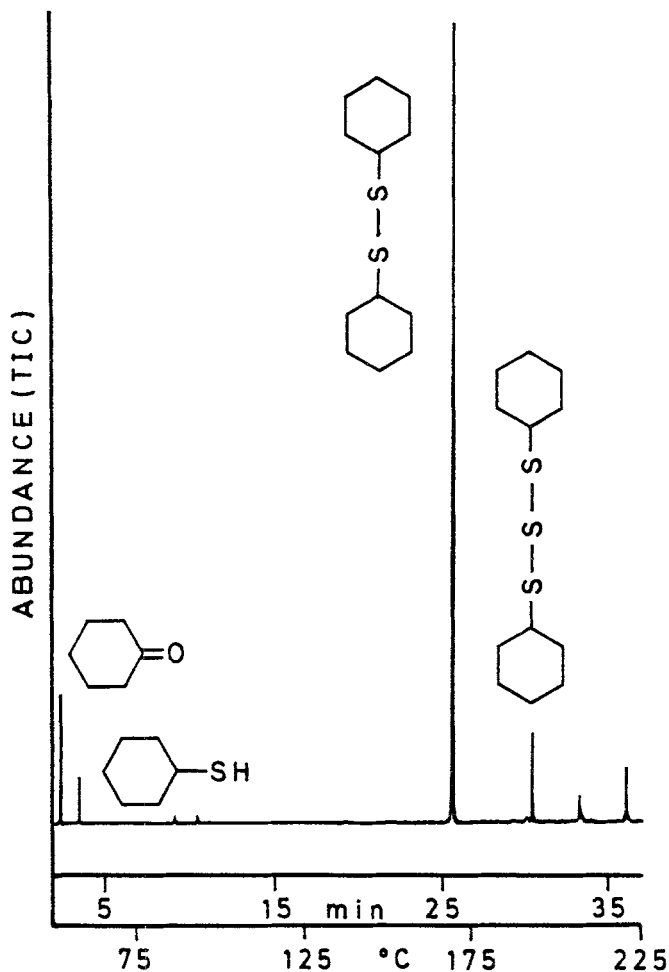


Fig. 2. Representation of the TIC trace of experiment R4. Some starting material remains. The main product is dicyclohexanedisulphide (P7). The two minor peaks with retention times longer than 31 min could not be identified by their MS patterns.

tically matched those of the FID chromatograms. Mass spectra (70 eV) were recorded in continuous scanning mode.

Results

Table I lists the main compounds (P1-P9) synthesized in the experiments. Tr (rel.) refers to the relative retention times (Ettre and Zlatkis, 1967, p. 375) from the TIC with respect to cyclohexanone (equal to 1). Also the main ions observed for each compound are listed in Table I. The molecular ion is underlined. The products were mainly identified from their mass spectral fragmentation patterns which was feasible as the number of possible products was limited. In most of the compounds

TABLE II
Experimental conditions and results of reactions R1(Fe)-R5(Fe)

Procedure	Temperature/ Time	Solvent	Conversion of cyclohexanone	Reduced com- pounds (% re- fers to total amount of products)	Condensed compounds (% refers to total amount of products)
R1(Fe) A	25 °C/4 hr	DMF	100%	P4 (<1%) P5 (8%) P7 (13%) <hr/> Total (21%)	P1 (78%)
R2(Fe) B	25 °C/4 d	DMF	95%	P4 (4%) P7 (81%) P8 (9%) <hr/> Total (94%)	
R3(Fe) B	25 °C/7 d	Methanol	80%	P4 (<1%) <hr/> Total (<1%)	P3 (40%) P2 (50%)
R4(Fe) B	100 °C/7 d	Methanol	90%	P4 (3%) P6 (1%) P7 (51%) P8 (3%) <hr/> Total (58%)	P3 (30%)
R5(Fe) B	100 °C/16 d	Methanol + DMF (2:1)	100%	P9 (15%) P6 (57%) P7 (19%) P8 (9%) <hr/> Total (100%)	

the M+2 ion (^{34}S isotope) was visible so that the number of sulphur atoms present could be estimated.

Figure 2 shows the TIC trace of one of the experiments (experiment R4(Fe)). The respective compounds (cyclohexanone, P4, P7 and P8) are also indicated. The two minor peaks at high retention times could not be identified by their fragmentation patterns.

Compounds P3, P7 and P9 were identified by the computer system through comparison with the incorporated NBS library. The identification of cyclohexanedithiol (P4) was confirmed by comparison with the authentic material.

The geminal cyclohexanedithiol (P1) and the dicyclohexyldisulphide (P7) were verified by $^1\text{H-NMR}$. In the case of P1 this was necessary as the dithiol loses H_2S on volatilisation in the GC injection port to yield the two corresponding tautomers; the thione and the enethiol (Mayer *et al.*, 1964). Thus two different retention times

are given in Table I for P1. Structures P2, P5, P6 and P8 were deduced from their fragmentation patterns.

In the case of P6 the ions at $m/z = 83, 80$ and 79 give strong evidence for the proposed structure; as do the ions at $m/z = 180, 115$ and 83 for the trisulphide (P8). The interpretation of the fragmentation pattern of P2 is more uncertain. It could possess an open structure or a closed ring system. Since the ring form tends to be stable we propose a 1,2,4-trithiolane structure for P2.

The analytical results of the FeS containing reactions are given in Table II. The abundances were obtained by computer integration of the TIC traces. In Table II the numbers are given for discrete experiments, since the number of replicate analyses are limited.

Reference to this Table reveals that P1 and P3 are synthesized by condensation of cyclohexanone with H₂S and methanol respectively. P3 occurs only when methanol is used as solvent. We consider P2 also to be a condensation product despite the oxidized disulphide moiety, because the carbonyl group is not reduced. The other products are reduced. Cyclohexyl-dimethylamine (P9) is a typical product in reactions where DMF is used as solvent at high temperatures as DMF decomposes to yield dimethylamine and carbon monoxide. Dimethylamine can react, for example, with cyclohexanethiol (P4) to yield P9. 1-Cyclohexyl-2-methyl-disulphide (P6) is a typical product in methanolic solutions and its formation can be explained from P5 and methanol by nucleophilic substitution. In the synthesis of P2, P5, P6, P7 and P8 an oxidation of sulphur has taken place.

The results for procedures performed in the absence of iron chloride are given in Table III.

Discussion

Firstly, we want to point out that in every reaction R1(Fe)-P5(Fe) reduced compounds were detected. In experiment R3(Fe) the total amount of reduced species (the amounts of reduced species are given in per cent with respect to the total amount of products) was lower than 1%. It is striking that the same reaction carried out in DMF (R2(Fe)) yielded almost entirely reduced compounds despite its shorter reaction time. One reason certainly is that in methanol the ketal (P3) is blocking the reduction, but this does not explain the large amounts of the trithiolane (P2) synthesised in R3(Fe). In the other reactions the amount of reduced compounds was much higher (R1(Fe), 21%; R4(Fe), 58%; R2(F2), 94% and R5(Fe), 100%). These results demonstrate that [FeS/FeS₂] is functioning as redox system. Furthermore we note that the amount of reduced compounds increases with time. In Table 2 this becomes clear by comparison of the reactions R1(Fe) and R2(Fe), which were carried out for 4 hours and for 4 days respectively. The yield of reduced products in R2(Fe) is remarkably higher (94%) than is reaction R1(Fe) (21%) although in the latter reaction excess of H₂S was used.

Yields of reduced compounds increase with increasing temperature. This becomes

TABLE III
Experimental conditions and results of reactions R1-R5, R6-R8

Procedure without FeCl ₂		Temperature/ Time	Solvent	Converted cyclohexanone	Reduced compounds (% refers to total of products)	Condensed compounds (% refers to total of products)
R1	A	25 °C/4 hr	DMF	55%	P4 (<1%) P5 (50%) Total (51%)	P1 (40%) P2 (9%)
R2	B	25 °C/4 d	DMF	5%	P8 (49%) Total (49%)	P1 (50%)
R3	B	25 °C/7 d	Methanol	32%	below detection limit	P1 (<1%) P3 (99%)
R4	B	100 °C/7 d	Methanol	55%	P4 (0.1%) P7 (<0.1%) P8 (<0.1%) Total (0.1%)	P3 (80%)
R6 ^a	C(i)	100 °C/1 d	Methanol + DMF (2:1)	98%	P4 (<0.1%) P9 (99%) P7 (<0.1%) Total (99%)	
R7 ^a	C(ii)	100 °C/1 d	Methanol + DMF (1:2)	100%	P4 (6%) P6 (12%) P7 (38%) P7 (14%) Total (70%)	P3 (17%) P3 (1%)
R8 ^a	C(iii)	100 °C/1 d	Methanol	100%	P4 (39%) P6 (21%) P7 (22%) P8 (10%) Total (92%)	

^a Percentages obtained from FID trace.

evident by comparison of reaction R3(Fe) with R4(Fe) which differ only in reaction temperature. The reaction carried out at room temperature (R3(Fe)) yields less than 1% of reduced species whereas in the case of R4(Fe), which was carried out at 100 °C, yields of reduced products higher than 90% are obtained. High temperature and long reaction time are realised which explains the exclusive synthesis of reduced molecules (yield of reduced compounds = 100%).

In all reactions with high yields of reduced species (R1(Fe), R2(Fe), R5(Fe)) the most abundant compounds are the disulphides P6 and P7. In reactions R1(Fe), R2(Fe) and R4(Fe) the proportion of dicyclohexyldisulphide (P7) of the *total amount*

of reduced products is 62, 86 and 54% respectively. In R5(Fe) the most abundant reduced compound is the cyclohexyl-methyl-disulphide (P6) due to involvement of methanol in the reaction. Here the yield of P6 and P7 with respect to the *total amount of reduced products* is 57% and 19% respectively. The high amounts of disulphides detected in these reactions are in agreement with our thermodynamical considerations (Figure 3).

The large amount of cyclohexyldisulphide (P5) in reaction R1(Fe) is striking. A plausible explanation is the short reaction time and the use of excess hydrogen sulphide. Both factors make, from the kinetic point of view, a reaction of cyclohexanethiol (P4) and H₂S more likely than a reaction between two molecules of cyclohexanethiol (P4) so that the thermodynamically more stable dicyclohexyldithiol (P7) is not synthesized. These considerations explain also that in cases where reactions were allowed a longer duration (R2(F2)-R4(Fe)) dicyclohexyldisulphide (P7) rather than cyclohexyldisulphide (P5) are detected, since with time, thermodynamic stability dominates kinetics i.e. metastable products are being transformed to stable products.

R5(Fe) is a special reaction. It is the only one where the two solvents are mixed. Therefore we obtained cyclohexyl-methyl-disulphide (P6), a typical product for methanol containing reactions, as well as cyclohexyldimethylamine (P9), a typical product for reactions where hot DMF is used. The synthesis of P9 is due to the decomposition of DMF to dimethylamine and carbon monoxide.

The results discussed above have demonstrated that the [FeS/FeS₂] redox system is capable of performing reductions. Also the influence of temperature, reaction time and the respective solvent on the reaction has been established. Further information concerning the reduction mechanism was obtained from work analogous to the above, but carried out in the absence of FeCl₂ · 4H₂O, i.e. the [FeS/FeS₂] redox system was replaced by the H₂S/S system. These results may be rationalised in relation to the total theme as follows:

(1) Experiments R1 and R1(Fe), that differ in only the abundance of Fe(II), lead to 51% and 21% of reduced compounds respectively. In other experiments, e.g. R4 and R4(Fe), the yield of reduced products of the [FeS/FeS₂] redox system was much higher than the yield of reduced products obtained by the H₂S/S redox system.

The H₂S/S redox system has been known for a long time (Mayer *et al.*, 1964; Hartman and Silloway, 1955; Fukunaga and Yamaguchie, 1981), but reductions of a single carbonyl group under our experimental conditions have not been reported previously. Mayer *et al.* (1963) were able to reduce 1,2-dicarbonyl compounds. Cairns *et al.* (1952) reduced cyclohexanone to dicyclohexyldisulphide (P7), but without solvent at 130 °C and 1000 bar.

The question that arises in the context of the [FeS/FeS₂] redox system is whether it is (at least in some experiments) the H₂S/S redox system within the [FeS/FeS₂] system or the authentic FeS/FeS₂ system that is responsible for the observed reactions. Here the detection of pyrite would distinguish between these possibi-

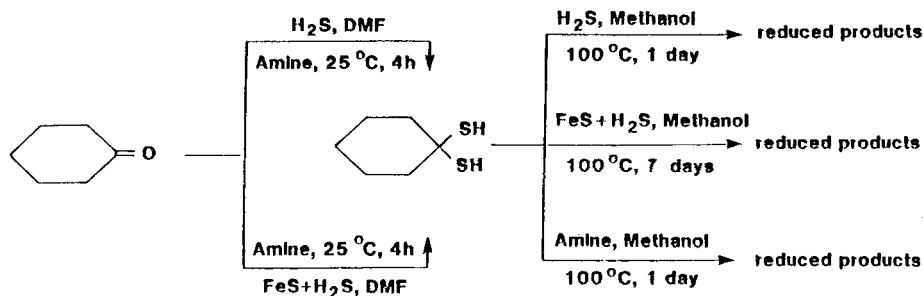


Fig. 3. Scheme illustrating the geminal cyclohexanedithiol (P1) as necessary intermediate on the pathway to the reduced product.

lities. We failed to identify pyrite by X-ray diffraction, but this may have been because of the amorphous nature of the precipitate. Transformation of any pyrite present to the corresponding disulfane and analyses by $^1\text{H-NMR}$ might resolve the question (Siebert, pers. comm. 1992).

(2) Experiments R6-R8 indicate that the geminal cyclohexanedithiol (P1) is a necessary intermediate for the synthesis of the reduced compounds. This hypothesis gives an explanation for the differences in products between R4 and R8 which were carried out under the similar conditions; owing to the formation of the ketal (P3) in R4 the formation of the geminal cyclohexanedithiol (P1) is suppressed which makes the synthesis of reduced products impossible, whereas in R8 the amount of reduced products exceeds 90%, since P1 is used as starting material. This hypothesis also explains why reaction R8 leads to reduced compounds without abundant ammonia, or primary or secondary amines, which catalyse the formation of P1.

(3) Experiment R7 shows that the geminal dithiol can even be reduced with only an amine at 100°C in methanol.

Figure 3 summarises our results concerning the reaction mechanism. The importance lies in the subdivision of the reaction in two steps (i) a condensation which leads to the dithiol (P1) and (ii) reductions that lead to the respective reduced products.

Conclusion

The results obtained by the reported experiments and their interpretation can be resumed as follows:

(1) The $[\text{FeS}/\text{FeS}_2]$ redox system is able to reduce the carbonyl group of the model compound cyclohexanone in all experiments apart from R3.

(2) Yields of reduced compounds are higher in DMF than in methanol especially at low temperatures due to the formation of the ketal (P3) in the latter.

(3) Yields of reduced products are higher with increasing temperature and duration.

(4) We propose that the geminal cyclohexanedithiol (P1) is a necessary intermediate for the reduced products. P1 can be reduced by the $\text{H}_2\text{S}/\text{S}$ and the $[\text{FeS}/\text{FeS}_2]$

system at 100 °C without abundant ammonia or amines. PI can also be reduced by dimethylamine alone.

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