Carbon Dioxide Fixation forming Oxazolidone coupled with a Thiol/Fe_4S_4 Cluster Redox System

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Carbon dioxide fixation reactions with ethanolamines to form oxazolidone derivatives have been investigated using 4Fe–4S ferredoxin analogues as the electron mediator.

Conversion of CO_2 into organic compounds is a major challenge in chemistry. Accordingly, a great deal of attention has been devoted to systems capable of fixing CO_2 electrochemically,[1] photochemically,[2] and chemically.[3,4] Of particular interest is the formation of useful materials of added value *via* fixation of CO_2. As an extension of our Fe_4S_4 work,[5] we have examined such reactions in detail with tetranuclear ferredoxin analogues[6] as the electron mediator. This paper describes successful CO_2 fixation forming 2-oxazolidones which are useful as anticonvulsant substances,[7] antibacterials,[8] fungicides,[9] synthetic reagents,[10] and so on.[11]

The system is composed of a MeCN solution (10 ml) that includes ethanolamine [(**1**), 4×10^{-2} M], thiol (8×10^{-3} M), phosphine (4×10^{-2} M), $(Et_4N)_2[Fe_4S_4(SPh)_4]$ [(**3**), 8×10^{-4} M] and triethylamine (6×10^{-2} M), and the reaction is carried out at 25 °C under *ca.* 10% O_2 in a CO_2 atmosphere. 2-Mercaptopyridine (PySH), 4-nitrothiophenol (NPSH), triphenylphosphine (Ph_3P), and tri-n-butylphosphine (Bu_3P) were used in this work. The rate of oxazolidone (**2**) formation as a function of time was followed by h.p.l.c. [octadecylsilane (ODS), $MeCN/H_2O = 40/60$, monitored at 250 nm]. A typical example is shown in Figure 1, where efficient formation of 5-phenyl-2-oxazolidone (**2a**) is illustrated with a (**1a**)/Ph_3P/PySH system. The chemical yield after 10 h and observed initial reaction rate were 88% and 7.6 mM/h, respectively. Employment of $FeCl_3$ showed less efficiency (the corresponding values were 44% and 2.4 mM/h), and no oxazolidone formed in the absence of an electron mediator.

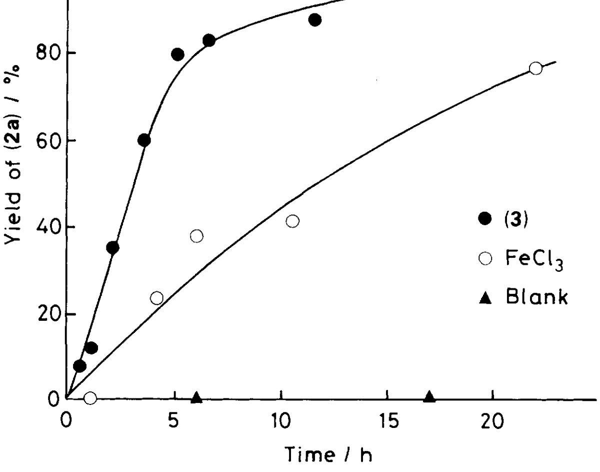
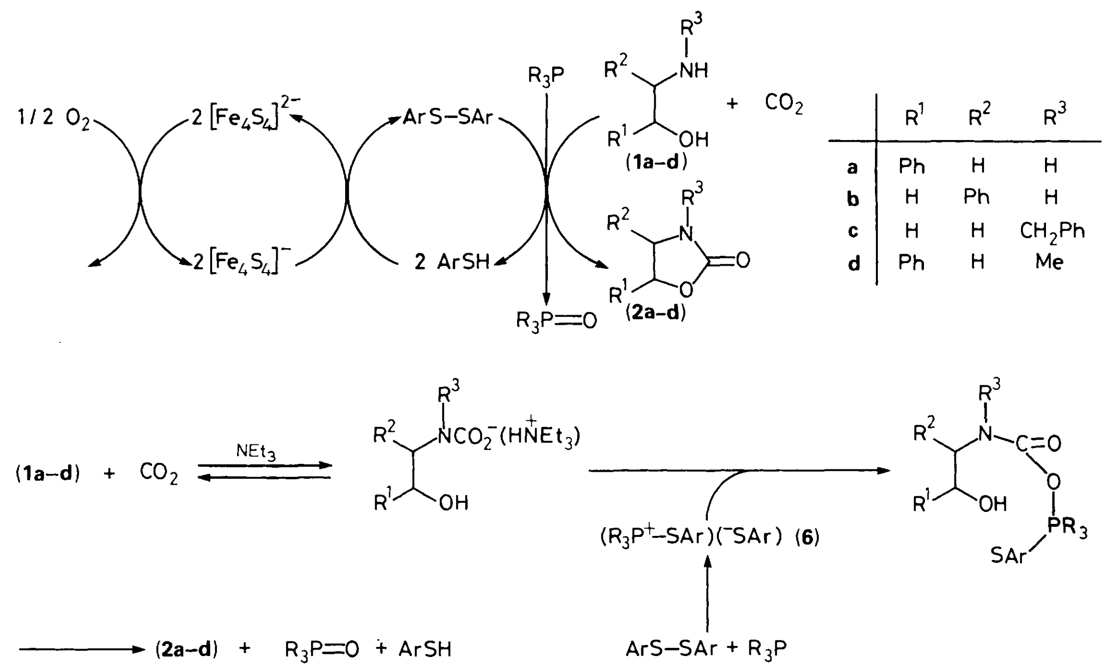


Figure 1. A time course of the yield of 5-phenyl-2-oxazolidone (**2a**) with a (**1a**)/PySH/$Ph_3P/CO_2/O_2$ system: [(**1a**)] = [Ph_3P] = 4.0×10^{-2} M; [NEt_3] = 6.0×10^{-2} M; [PySH]/[(**1a**)] = 1/5; [(**3**)]/[(**1a**)] = [$FeCl_3$]/[(**1a**)] = 1/50; 25 °C in MeCN.

Table 1 summarizes the yield of 2-oxazolidone derivatives (**2a**—**d**) with the four systems according to various combina-



	R^1	R^2	R^3
a	Ph	H	H
b	H	Ph	H
c	H	H	CH$_2$Ph
d	Ph	H	Me

Scheme 1. Estimated reaction scheme for the CO$_2$ fixation.

tions of thiols and phosphines. Notably, as a whole the yield is remarkably higher in the presence of the Fe$_4$S$_4$ cluster than in the presence of FeCl$_3$ or in the absence of the Fe compound. This suggests that the Fe$_4$S$_4$ complex is an excellent catalyst for the system. Previous studies have shown that the Fe$_4$S$_4$ cluster markedly catalyses the oxidation of thiol by oxygen.[12] Eventually, prior to the CO$_2$ experiment, we have confirmed that the cluster (**3**) catalyses PySH to PySSPy at a rate of 50 mM/h, but the rate decreases two orders of magnitude with FeCl$_3$ (0.17 mM/h) or without catalyst (0.11 mM/h). It was also proved that 2-oxazolidones were readily obtained in the presence of disulphides and phosphines from the ethanolamine derivatives and CO$_2$. Subsequent $O_2{}^{\bullet-}$ formation has been shown.[12]

Table 1. Yield of 2-oxazolidone derivatives (**2a**—**d**).[a]

	Yield/%			
	(**2a**)	(**2b**)	(**2c**)	(**2d**)
Ph$_3$P/PySH				
Fe–S	88 (8)[b]	18 (6)	42 (3)	15 (1)
FeCl$_3$	44 (2)	12 (1)	28 (2)	15 (1)
Blank[c]	0	0	0	0
Bu$_3$P/PySH				
Fe–S	70 (16)	63 (11)	40 (10)	21 (6)
FeCl$_3$	47 (5)	21 (2)	19 (1)	4 (0)
Blank	0	0	0	0
Ph$_3$P/NPSH				
Fe–S	31 (3)	14 (2)	16 (1)	5 (0)
FeCl$_3$	13 (1)	7 (1)	13 (1)	5 (0)
Blank	8 (1)	6 (0)	11 (1)	5 (0)
Bu$_3$P/NPSH				
Fe–S	80 (27)	68 (20)	39 (13)	18 (4)
FeCl$_3$	50 (4)	37 (4)	11 (1)	6 (0)
Blank	19 (1)	17 (1)	6 (1)	6 (0)

[a] [Fe–S]/[Substrate] = [FeCl$_3$]/[Substate] = 1/50; h.p.l.c. yield (%) after 10 h. [b] Values in parentheses are initial reaction rates (mM/h). [c] In the absence of electron mediator.

In view of these observations, we suggest the schematic cycle outlined in Scheme 1 as the multi-step process leading to the formation of 2-oxazolidone as well as the estimated reaction mechanism. Thus the results obtained in this work allow us to mention the following features. (i), With the Bu$_3$P systems, both the initial reaction rate and the yield of 2-oxazolidones (**2a**—**d**) are in the order of **a** > **b** > **c** > **d**. (ii), With Ph$_3$P systems, however, the rates are in the same order, while yields are **a** > **c** > **b** > **d**. (iii), The Bu$_3$P system generally gives higher yield and a larger initial rate than the Ph$_3$P system. (iv), Yields are specially lower with NPSH than with PySH in the Ph$_3$P system, whereas on the contrary NPSH gives a little higher reactivity than PySH with the Bu$_3$P system.

MNDO (modified neglect of diatomic overlap method) calculations suggest that stability of the corresponding carbamates (**4**) is in the order of **a** > **b** > **c** > **d**, which is as a whole in good agreement with the present experimental findings [(i) and (ii)]. A clear explanation for the exceptionally low yield of (**2b**) with a Ph$_3$P/PySH system is so far unavailable. We have evidence that the formation of PyS$^-$ [$\lambda_{max.}$ (ε) nm in MeCN; 290 (16200), 372 (6380)] is remarkably fast in the reaction of PySSPy and Bu$_3$P, but is very slow with Ph$_3$P (Scheme 1). Therefore, the result in (iii) may be accountable by the difference in nucleophilic properties of the phosphines. Namely, stronger nucleophilicity of Bu$_3$P[13] than Ph$_3$P towards disulphide leads to feasible formation of (**6**),[14] while weaker nucleophilicity of Ph$_3$P is unfavourable for the intermediate formation. The result in (iv) may be interpreted as follows. In the Bu$_3$P system the overall yield may be governed by oxidation rates of the thiols, since NPSH is more easily oxidized than PySH, the details of which, including n.m.r. spectroscopic studies, will be reported elsewhere.

Conclusively, we have accomplished CO$_2$ fixation into useful organic compounds, 2-oxazolidone derivatives.

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