

## Oxidation and Oxidative Carbonylation of Methane and Ethane by Hexa-oxo- $\mu$ -peroxodisulfate(2-) Ion in Aqueous Medium. A Model for Alkane Oxidation through the Hydrogen-atom Abstraction Pathway

Minren Lin and Ayusman Sen\*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

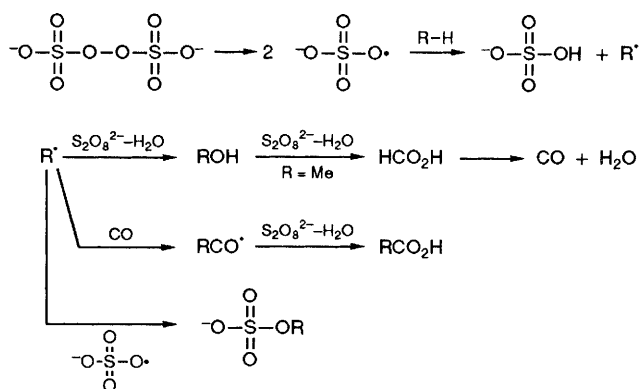
In aqueous medium, at 105–115 °C,  $\text{SO}_4^{\cdot-}$  (generated from  $\text{S}_2\text{O}_8^{2-}$ ) was found to abstract a hydrogen atom from methane and ethane to form the corresponding alkyl radicals which could be trapped efficiently by carbon monoxide, the resultant acyl radicals being ultimately converted into the homologous carboxylic acids.

Methane is the most abundant and the least reactive member of the hydrocarbon family (C–H bond energy: 435 kJ mol<sup>-1</sup>). Ethane comes second in both categories. Hence, C–H activation leading to selective oxidation of these hydrocarbons is one of the most challenging chemical problems, in addition to being of great practical importance. One possible C–H activation pathway involves hydrogen-atom abstraction by a metal-oxo radical that results in the formation of the corresponding alkyl radical [eqn. (1)]. For methane, this



pathway is believed to operate in the enzyme, methane monooxygenase,<sup>1</sup> and in the high-temperature coupling of

methane on metal oxides.<sup>2</sup> However, hydrogen-atom abstraction from methane has never been directly observed *in vitro* under mild, thermal, conditions. The principal problem is that the methyl radical is a particularly high-energy species and, indeed, the step shown in eqn. (1) has been observed for hydrocarbons possessing significantly weaker secondary and tertiary C–H bonds.<sup>3</sup> Herein, we describe our observations on the oxidation and oxidative carbonylation of methane and ethane by hexa-oxo- $\mu$ -peroxodisulfate(2-) ion which proceeds through a closely analogous hydrogen-abstraction pathway. Apart from serving as the first mild, solution phase, model for hydrogen abstraction from methane and ethane by an oxo radical, these observations constitute the first examples of



Scheme 1

oxidative carbonylation of these hydrocarbons resulting in one-pot synthesis of homologous aliphatic carboxylic acids.

The hexaoxo- $\mu$ -peroxodisulfate(2-) ion is a strong oxidant, with the standard reduction potential for the  $S_2O_8^{2-}/SO_4^{2-}$  couple estimated to be 2 V in aqueous solution.<sup>4</sup> Upon mild thermolysis, O-O bond homolysis is known to occur to yield the radical,  $SO_4^{\cdot-}$  (Scheme 1). While the reaction of the latter species with arenes and alkenes has been studied in detail,<sup>5</sup> we are unaware of any report concerning its use in the oxidation of the lower alkanes. Our results on the reaction of  $K_2S_2O_8$  with methane and ethane in water in the presence and absence of added carbon monoxide are summarized in Table 1. In the case of methane, when the reaction was stopped after only 3 h, the observed products<sup>†</sup> were  $MeOSO_3^-$ ,  $MeOD$ ,  $HCO_2D$ , and  $MeCO_2D$  in the ratio of 3.2:1.1:1.0:14.5 (combined yield: 3% relative to  $K_2S_2O_8$ ). At longer reaction times,  $MeCO_2D$  was the only observed organic product.  $MeOSO_3^-$  was found to hydrolyse slowly to  $MeOD$ , and presumably at longer reaction times, the latter was further oxidized to  $HCO_2D$  which, in turn, decomposed to carbon monoxide and water. The most curious facet of the reaction of methane with  $K_2S_2O_8$  was the formation of acetic acid, a two carbon containing molecule. A possible scenario is illustrated in Scheme 1. Following generation of methyl radical by hydrogen abstraction, some of it was converted sequentially into methanol, formic acid and, finally, carbon monoxide and water. The carbon monoxide, thus formed, efficiently trapped other methyl radicals (rate:  $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )<sup>6</sup> to form the acetyl radical which was further converted into acetic acid. There are three pieces of evidence in support of this mechanism. First, as illustrated in Table 1, a dramatic increase in the formation of acetic acid was observed when the oxidation of methane was carried out in the presence of carbon monoxide. Secondly, an increase in the formation of acetic acid was also observed upon the addition of formic acid to the reaction mixture. Lastly, in the presence of  $^{13}CO$ ,  $Me^{13}CO_2D$  was formed.<sup>‡</sup>

The results obtained from the reaction of ethane with  $K_2S_2O_8$  are also shown in Table 1. The principal difference between the reaction of methane and ethane in the absence of added carbon monoxide was that while formic acid decomposed readily to carbon monoxide and water, acetic acid was more stable. Therefore, a significant yield of acetic acid was observed with ethane and, furthermore, there was no homoligation to propionic acid. That the reaction of ethane with  $K_2S_2O_8$  also proceeded through an intermediate alkyl radical was shown by the formation of propionic acid as the principal

Table 1

Substrate (psi) <sup>a</sup>	Products (% yield) <sup>b,c</sup>
$CH_4$ (1000)	$MeCO_2H$ (5.5)
$CH_3CH_3$ (550)	$MeCO_2H$ (16.2), $EtOSO_3^-$ (20.3)
$CH_4$ (1000)/ $HCO_2H$ (1 mmol)	$MeCO_2H$ (13.6)
$CH_4$ (700)/ $CO$ (300)	$MeCO_2H$ (48.6)
$CH_3CH_3$ (550)/ $CO$ (500)	$MeCO_2H$ (2.5), $MeCH_2CO_2H$ (40.8)

<sup>a</sup> 1 psi  $\approx 6.894 \times 10^3$  Pa. <sup>b</sup> Conditions:  $K_2S_2O_8$  (0.74 mmol),  $D_2O$  (4 cm<sup>3</sup>), 105–115 °C; 10–16 h. <sup>c</sup> Yield relative to  $K_2S_2O_8$ .

product when carbon monoxide was introduced into the system. Evidently, the trapping of ethyl radical by carbon monoxide was significantly faster than its further oxidation by the hexaoxo- $\mu$ -peroxodisulfate(2-) ion.

Finally, as expected, the homolysis of a weaker secondary C-H bond was the dominant pathway when propane was the substrate. Analogous to the reactions with methane and ethane, homologation to isobutyric acid occurred upon the addition of carbon monoxide.

In conclusion, the first mild, solution phase, example of hydrogen abstraction from methane and ethane by an oxo radical has been discovered. In addition, our observations constitute the first examples of oxidative carbonylation of these lower alkanes in solution. Since the hexaoxo- $\mu$ -peroxodisulfate ion is commercially produced by electrooxidation of the sulfate ion,<sup>7</sup> in principle it should be possible to use the hexaoxo- $\mu$ -peroxodisulfate ion as a catalyst for the electro-oxidation of methane and ethane to useful organic products.

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## References

- 1 J. Green and H. Dalton, *J. Biol. Chem.*, 1989, **264**, 17698; F. Ruzicka, D.-S. Huang, M. I. Donnelly and P. A. Frey, *Biochemistry*, 1990, **29**, 1696; also see: A. S. Golstein and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1991, 21.
- 2 *Catal. Today*, 1989, **4**; J. H. Lunsford, *Catal. Today*, 1990, **6**, 235; G. H. Hutchings, M. S. Scurrall and J. R. Woodhouse, *Chem. Soc. Rev.*, 1989, **18**, 251; G. H. Hutchings, J. R. Woodhouse and M. S. Scurrall, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2507.
- 3 Recent reviews and representative examples: (a) S. E. Groh and M. J. Nelson, in *Selective Hydrocarbon Activation*, ed. J. A. Davies, P. L. Watson, J. F. Liebman and A. Greenburg, VCH, New York, 1990, p. 305; (b) J. T. Groves, *J. Chem. Ed.*, 1985, **62**, 928; (c) F. P. Guegerich and T. L. Macdonald, *Acc. Chem. Res.*, 1984, **17**, 9; (d) T. G. Traylor, *Pure Appl. Chem.*, 1991, **63**, 265; (e) P. E. Ellis and J. E. Lyons, *Coord. Chem. Rev.*, 1990, **105**, 181; (f) D. Mansuy and P. Battioni, in *Activation and Functionalization of Alkanes*, ed. C. L. Hill, Wiley, New York, 1989, p. 195; (g) K. S. Suslick, in ref. 3(f), p. 219; (h) C. L. Hill, in ref. 3(f), p. 243; (i) D. H. R. Barton and N. Ozbalik, in ref. 3(f), p. 281; (j) C. A. Tolman, J. D. Druliner, M. J. Nappa and N. Herron, in ref. 3(f), p. 303; (k) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1988, **110**, 8628; (l) K. Srinivasan, P. Michand and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309; (m) D. Mansuy, J.-F. Bartoli, P. Battioni, D. K. Lyon and R. G. Finke, *J. Am. Chem. Soc.*, 1991, **113**, 7222.
- 4 W. M. Latimer, *Oxidation States of Elements and Their Potentials in Aqueous Solution*, Prentice-Hall, New York, 1952, p. 78.
- 5 Review: F. Minisci, A. Citterio and C. Giordano, *Acc. Chem. Res.*, 1983, **16**, 27.
- 6 A. Bakac and J. H. Espenson, *J. Chem. Soc., Chem. Commun.*, 1991, 1497.
- 7 *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, Wiley, New York, 1985, p. 846.

<sup>†</sup> Products were identified and quantified by NMR spectroscopy. In some cases the spectra were compared with authentic samples. <sup>1</sup>H NMR ( $D_2O$ ),  $\delta$  3.66 (3 H, s,  $MeOSO_3^-$ ); 3.21 (3 H, s,  $MeOD$ ); 8.15 (1 H, s,  $HCO_2D$ ) and 1.94 (3 H, s,  $MeCO_2D$ ).

<sup>‡</sup> <sup>1</sup>H NMR ( $D_2O$ )  $\delta$  1.94 (3 H, d,  $J_{C,H}$  6.6 Hz).