JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 167–173

Electrochemical oxidation of aliphatic hydrocarbons promoted by inorganic radicals. I. OH radicals

RENATO TOMAT

*Istituto di Polarografia ed Elettrochimica, Preparativa del CNR, Corso Stati Uniti 4,
35100 Padova, Italy*

ADELIO RIGO

Istituto di Patologia Generale – Università di Padova, Via Loredan 16, 35100 Padova, Italy

Received 8 February 1984; revised 21 May 1984

The OH initiated oxidation of aliphatic hydrocarbons by the simultaneous electrochemical reduction of O_2 and of Fe(III) at controlled potential was investigated in the liquid phase over a Fe(III) concentration range 0.5–5 mM. OH radicals were generated by the reaction:

$$\mathrm{Fe(II)} + H_2O_2 \longrightarrow \mathrm{Fe(III)} + {}^{\cdot}OH + OH^-$$

The compounds studied were the linear alkane hydrocarbons from C_5 to C_{10} and 3-methyl pentane. The results showed that the ketones are the only reaction products and that the yields decrease with increasing number of carbonium atoms of the hydrocarbon. Decreasing yields were also observed with increasing Fe(III) concentration.

---

1. Introduction

We have shown that OH radicals generated during the electrochemical reduction of oxygen and of Fe(III) can be utilized in the oxidation of aromatic hydrocarbons [1–4]. Under similar conditions we found that cyclohexane is oxidized to cyclohexanone with high yields [5].

However, in the case of aliphatic hydrocarbons limited information is available on their oxidation in the liquid phase, by OH radicals.

In the present work a systematic study of reactions involving OH radicals and aliphatic hydrocarbons was performed by controlled potential electrolysis, in view of its attractive synthetic significance.

2. Experimental procedures

OH radicals were obtained from the reduction of H_2O_2 by the Fe(II)/Fe(III) redox couple. Hydrogen peroxide was produced by electrolytic reduction of molecular oxygen saturating the solutions. The reduction of Fe(III) ions (occurring at nearly the same cathodic potential as O_2 reduction) allowed the recovery of the reduced form of the redox couple.

The chemicals used were reagent grade products; water and mercury were twice distilled.

The electrochemical cell was equipped with a platinum counter electrode and a saturated calomel electrode as reference; the cathode was a mercury pool of about 10 cm^2 surface area. The cathodic compartment, separated from the anodic by a salt bridge, was filled with 10 cm^3 of the hydrocarbon, 15 cm^3 of *tert*-butyl alcohol and 2 cm^3 of 12 N HCl, to which small amounts ($\leqslant 0.5$ cm^3) of 0.29 M Fe^{3+} solution containing HCl were added. In the case of C_8–C_{10} hydrocarbons, to avoid phase separation, 8 cm^3 of alkane and 17 cm^3 of *tert*-BuOH were utilized. During the electrolysis the solution was stirred at a constant rate by a magnetic stirrer and was kept saturated with O_2 by bubbling high purity

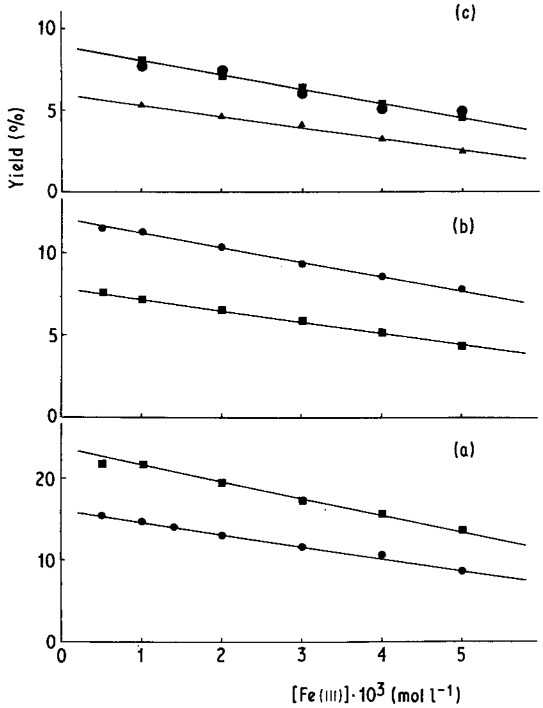


Fig. 1. Current yields of ketones against Fe(III) concentration. (a) ■ – 2-pentanone, ● – 3-pentanone, $t = 20°$; (b) ■ – 2-hexanone, ● – 3-hexanone, $t = 30°$; (c) ■ – 2-heptanone, ● – 3-heptanone, ▲ – 7-heptanone, $t = 30°$.

oxygen through the solution. After electrolysis ($E = -0.5$ V vs SCE) the solution was neutralized with $NaHCO_3$ and analysed by gas phase chromatography by a Fractovap model 4160 gas chromatograph (C. Erba, Milan). The chromatographic column, 25 m FFAP/0.3 mm i.d., H_2 as a carrier gas at 1.5 $cm^3 min^{-1}$, was operated with the following temperature programme: 50° C for 5 min, then at 2° $C min^{-1}$ to 80° C for 10 min.

The 'on column injection' of the sample was adopted for a better analytical response.

In the case of *n*-pentane the column was 50 m of OV 17/0.3 mm i.d., operating at 50° C with H_2 as a carrier gas at 1.5 $cm^3 min^{-1}$.

The internal standards used in the quantitative determination of the products were: 1-pentanol for pentane, 1-hexanol for hexane, heptane and decane, 1-heptanol for octane and nonane, cyclohexanone fo 3-methyl pentane.

3. Results

The gas chromatographic and gas chromatographic–mass spectra analyses of the reaction mixtures showed that ketones are the only detectable reaction products of the electrochemical oxidation of *n*-alkanes characterized by 5–10 carbon atoms and of 3-methyl pentane. A general feature of this process is the linear decrease of the yields with increase in the concentration of Fe(III) ions from 0.5 to 5 mM, see Figs. 1, 2, where the yields of the different ketones obtained from the examined alkanes were reported. The yields were calculated on the basis of 3 Faradays of electricity per mole of produced ketones (see Reactions 1 and 2). The current yields of ketone were about 40% in the case of pentane and about 6% in the case of decane and decrease almost monotonically with the number of carbon atoms present in the hydrocarbon, see Fig. 3. The decrease of the yields with increasing Fe(III) concentration was explained as due to a loss of current for the in-excess production of Fe(II) [1–5]. Since the yields are dependent on the Fe(III) concentration, the molar ratios of the isomeric ketones were calculated from the experimental curves of Figs. 1 and 2. From these calculations there appears to be a slight dependence of the ratios on the Fe(III) concentration.

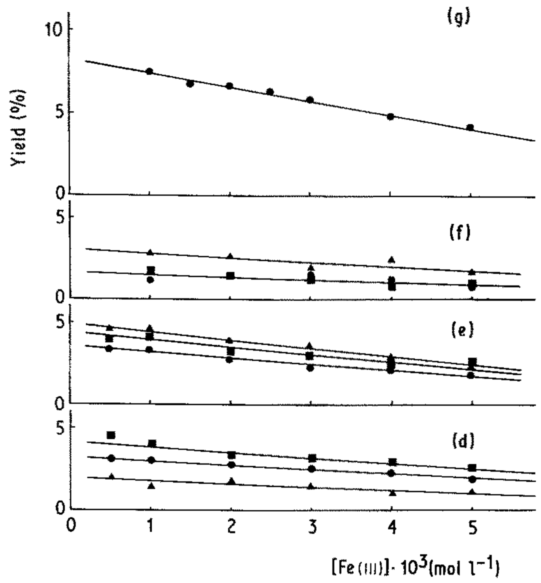


Fig. 2. Current yields of ketones against Fe(III) concentration. (d) ■ – 2-octanone, ● – 3-octanone, ▲ – 4-octanone, $t = 30°$; (e) ■ – 2-nonanone, ● – 3-nonanone, ▲ – 4-plus 5-nonanone, $t = 30°$; (f) ■ – 2-decanone, ● – 3-decanone, ▲ – 4-plus 5-decanone, $t = 30°$; (g) ● – 3-methyl-2-pentanone, $t = 30°$.

In Table 1 the experimental ratios obtained at 1 mM and 5 mM Fe(III) are reported. Table 1 also reports the molar ratios calculated on the bases of the number of secondary carbon atoms whose oxidation produce the different ketones, assuming an equal reactivity for all the CH_2 groups. Some deviations from the expected values were found; in particular for C_5–C_7 alkanes the formation of 2 and 4 isomers appears favoured in comparison with 2 isomer, while in the case of C_8–C_{10} the formation of 2 isomer appears favoured.

In the case of 3-methyl pentane, notwithstanding the high reactivity of the tertiary carbon atom, the only product was the 3-methyl 2-pentanone, with a yield of 7.5% at[Fe(III)] = 1 mM. This yield was surprisingly low if compared with the yield of 2-pentanone obtained in the oxidation of pentane.

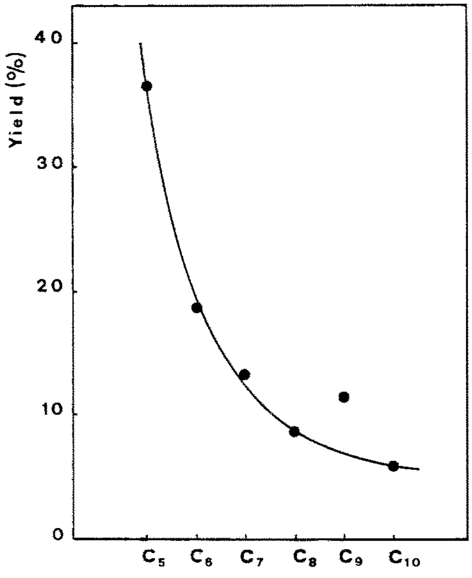


Fig. 3. Total current yields of isomeric ketones obtained at [Fe(III)] = 10^{-3} mol dm^{-3}.

Table 1. Experimental molar ratios of isomeric ketones at different Fe(III) concentrations. On the right hand column theoretical ratios are reported

Ketone	*Molar ratios*		*Theoretical ratios*
	[Fe(III)] = 1 mM	*[Fe(III)] = 5 mM*	
2-pentanone	0.60	0.60	0.67
3-pentanone	0.40	0.40	0.33
2-hexanone	0.39	0.37	0.50
3-hexanone	0.61	0.63	0.50
2-heptanone	0.38	0.39	0.40
3-heptanone	0.38	0.39	0.40
4-heptanone	0.24	0.22	0.20
2-octanone	0.44	0.45	0.33
3-octanone	0.35	0.36	0.33
4-octanone	0.21	0.19	0.33
2-nonanone	0.34	0.34	0.286
3-nonanone	0.28	0.28	0.286
4-nonanone 5-nonanone	0.38	0.38	0.428
2-decanone	0.26	0.265	0.25
3-decanone	0.26	0.265	0.25
4-decanone 5-decanone	0.48	0.47	0.50

4. Discussion

In the course of the electrolysis the processes occurring in the cathodic compartment of the electrolytic cell can be schematized as follows:

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2 \qquad (1)$$

$$\mathrm{Fe(III)} + e \longrightarrow \mathrm{Fe(II)} \qquad (2)$$

$$\mathrm{Fe(II)} + H_2O_2 \xrightarrow{k_3} \mathrm{Fe(III)} + {}^{\cdot}OH + OH^- \qquad (3)$$

$${}^{\cdot}OH + \mathrm{Fe(II)} \xrightarrow{k_4} OH^- + \mathrm{Fe(III)} \qquad (4)$$

$${}^{\cdot}OH + \text{hydrocarbon} \xrightarrow{k_5} \text{products} \qquad (5)$$

Other concurrent reactions are:

$${}^{\cdot}OH + \textit{tert}\text{-BuOH} \xrightarrow{k_6} \text{products} \qquad (6)$$

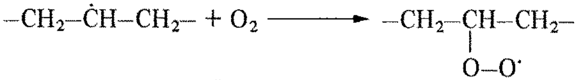
$${}^{\cdot}OH + Cl^- \xrightarrow{k_7} OH^- + Cl^{\cdot} \qquad (7)$$

where $k_3 = 76 M^{-1} s^{-1}$ [6]; $k_4 = 3 \times 10^8 M^{-1} s^{-1}$ [6]; $k_6 = 5.7 \times 10^8 M^{-1} s^{-1}$ [6]; $k_7 = 4 \times 10^9 M^{-1} s^{-1}$ at pH = 0 [7].

The kinetic rate constants of the reaction of OH radicals with hydrocarbons, k_5, measured in the gas phase are as follows ($k \times 10^{-9} M^{-1} s^{-1}$): *n*-pentane 2.2 at 27° C [8]; *n*-hexane 3.8 at 32° C [9]; *n*-heptane 3.7 at 27° C [8]; *n*-nonane 5.8 at 27° C [8]; *n*-decane 5.8 at 27° C [8]; 3-methyl pentane 4.3 at 32° C [9]. However, according to different authors [10, 11] the kinetics of Reaction 5 in the liquid phase would be faster. As regards the nature of this reaction, it is known since the pioneering work of Greiner [12, 13] that hydroxyl radicals react with alkanes abstracting H atoms and producing H_2O and an alkyl radical:

$$\cdot OH + -CH_2-CH_2-CH_2- \longrightarrow H_2O + -CH_2-\dot{C}H-CH_2- \quad (8)$$

In the presence of molecular oxygen the alkyl radicals formed in Reaction 8 add oxygen at very high rates [14] with the formation of alkyl peroxy radicals:



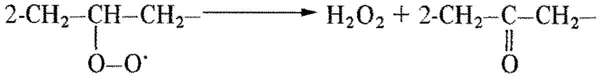
$$-CH_2-\dot{C}H-CH_2- + O_2 \longrightarrow -CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \quad (9)$$

which were identified by ESR techniques [15].

The fate of alkyl peroxy radicals is a process studied by many authors (see the recent study by Schuchmann and von Sonntag [16] and the references quoted) and, on the basis of the nature of the products we have obtained, can be schematically depicted by the following main group of reactions.

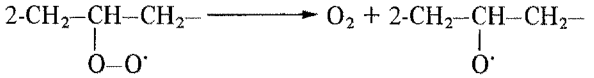
4.1. *Bimolecular self reactions*

Such reactions are (see [17, and 18])



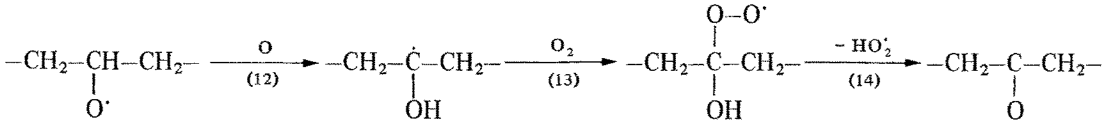
$$2\text{-}CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \longrightarrow H_2O_2 + 2\text{-}CH_2-\underset{O}{\underset{\|}{C}}-CH_2- \quad (10)$$

and



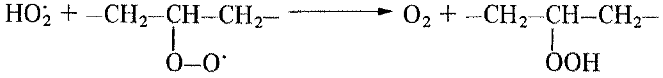
$$2\text{-}CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \longrightarrow O_2 + 2\text{-}CH_2-\underset{O\cdot}{\underset{|}{C}H}-CH_2- \quad (11)$$

The alkoxy radicals react further with formation of the corresponding ketones:



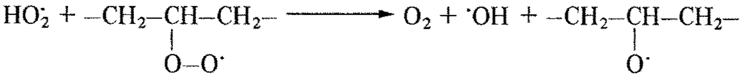
$$-CH_2-\underset{O\cdot}{\underset{|}{C}H}-CH_2- \xrightarrow[(12)]{O} -CH_2-\underset{OH}{\underset{|}{\dot{C}}}-CH_2- \xrightarrow[(13)]{O_2} -CH_2-\overset{O-O\cdot}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2- \xrightarrow[(14)]{-HO_2^{\cdot}} -CH_2-\underset{O}{\underset{|}{C}}-CH_2-$$

(see [19, 20]). Furthermore, the $HO_2^{\cdot}$ species generated in this process can be easily subtracted from the reaction system by the following reactions [16]:



$$HO_2^{\cdot} + -CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \longrightarrow O_2 + -CH_2-\underset{OOH}{\underset{|}{C}H}-CH_2- \quad (15)$$

$$HO_2^{\cdot} + -CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \longrightarrow O_2 + H_2O + -CH_2-\underset{O}{\underset{\|}{C}}-CH_2- \quad (16)$$

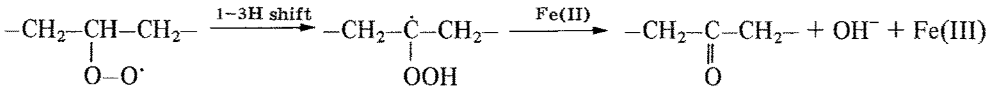


$$HO_2^{\cdot} + -CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \longrightarrow O_2 + \cdot OH + -CH_2-\underset{O\cdot}{\underset{|}{C}H}-CH_2- \quad (17)$$

The alkyl hydroperoxides produced in Reaction 15 may be converted by Fe(II) ions to the corresponding alkoxy radicals [21, 22] which react according to the reaction of sequence of Equations 12–14.

4.2. *Intramolecular H shift*

This is a peculiar liquid phase rearrangement of unstable radicals (for an exaustive review of this field see the article by Freidlina and Terent'ev [23]). In our case a possible type of rearrangement and stabilization of the alkyl peroxy radicals would be the following:



$$-CH_2-\underset{O-O\cdot}{\underset{|}{C}H}-CH_2- \xrightarrow{\text{1-3H shift}} -CH_2-\underset{OOH}{\underset{|}{\dot{C}}}-CH_2- \xrightarrow{Fe(II)} -CH_2-\underset{O}{\underset{\|}{C}}-CH_2- + OH^- + Fe(III) \quad (18)$$

Greiner [13] and Darnall *et al.* [8] from the analysis of a number of experimental data on the reactivity of OH radicals toward a set of alkanes in the gas phase found a relation correlating the rate constant (k_{obs}) for the abstraction of H atoms with the structure, that is, with the number of primary (N_{prim}), secondary (N_{sec}) and tertiary (N_{tert}) H atoms in the molecule. This relation may be expressed as:

$$k_{obs} = AN_{prim} + BN_{sec} + CN_{tert} \tag{19}$$

Since the B value is about ten times higher than that of A, it follows that primary alkyl radicals would be formed with a maximum percentage of about 9% in the case of pentane and of about 3.5% in the case of decane.

Therefore according to Equation 19 and because the oxygen insertion occurs at the site where the H atoms were abstracted, the relative per cent yields of the isomeric ketones will depend on the number of equivalent hydrogen atoms present in the hydrocarbon molecule. The experimental data seem to support the above considerations. In fact, only very small amounts of aldehydes have been detected in some experiments and the experimental yields of the isomeric ketones are roughly in accord with the expected ones, see Table 1. However, an inspection of Table 1 data indicates some deviations which cannot be accounted for by the experimental errors. For instance the ratio of theoretical yield: experimental yield for the 2-ketone appears to increase with the length of the aliphatic chain while, conversely, the above ratio for the 3-isomer decreases on increasing the length of the aliphatic chain. These systematic deviations may indicate that other mechanisms beyond those described by Equations 10–18 could operate under our experimental conditions. Other evidence that the reactivity of the alkyl radicals may be influenced by the nature of the components of the reaction media is the decrease of the total ketones yield with increasing molecular weight of the hydrocarbons (see Fig. 3), while according to the aforesaid kinetic rate constants and to the relative concentrations of hydrocarbons no significant changes of reactivity are expected. This decrease cannot be easily explained. It must be remarked that all the experiments have been carried out under homogeneous conditions and that impurities are not involved in the observed decrease of the yield. In fact the same results were obtained after hydrocarbon distillation by a 30-plate adiabatic distillation column. In particular, the contribution of the reaction

$$\mathrm{Cl^{\cdot}} + \text{hydrocarbon} \longrightarrow \mathrm{HCl} + \text{alkyl radical} \tag{20}$$

should be considered since at least a quarter of the OH radicals generated in Reaction 3 react with Cl^- ions to produce Cl atoms.

The formation of chlorine atoms enhances greatly the yield of oxidized products of cyclohexane (Cl^- effect) [16]. In this case experimental demonstration of the existence of this effect is not easy. In fact, the use of H_2SO_4 or $HClO_4$ as a substitute for HCl was hindered by the low electrolytic conductivity obtained in the solution, while the addition of HBF_4 or HPF_6 to the *tert*-BuOH–hydrocarbon system cause a dramatic decrease of the yield and only traces of ketones are produced. The lower total yields with respect to those obtained with aromatic hydrocarbons [1–4] could be ascribed to the wastage of OH radicals through Reaction 6 which contributes to subtract OH radicals from the reaction system. Taking into account the relative molar concentrations of hydrocarbon, Cl^-, *tert*-BuOH and their reactivities towards OH radicals, about a quarter of the OH radicals generated in Reaction 3 are wasted by parasitic reaction with the alcohol. In particular, 2-propanone, which is produced by Reaction 6 [18], was identified in the course of some experimental runs.

In conclusion, our experimental results indicate that in the liquid phase OH radicals react at appreciable rate with alkanes, when the latter are homogeneously dissolved in the reaction media. The abstraction of hydrogen atoms makes possible the activation of the hydrocarbon molecule towards molecular oxygen and, as a consequence, the insertion of a carbonyl function on the alkane. The process is characterized by high selectivity and by mild operative conditions, and from this point of view could be proposed as an alternative to the usual preparative chemical methods. Additional work is in progress to optimize the electrical and volume yields.

Acknowledgement

We thank Mr Romeo Salmaso of the Italian National Research Council – CNR – for his helpful support in the experimental work.

References

[1] R. Tomat and E. Vecchi, *J. Appl. Electrochem.* **1** (1971) 185.
[2] R. Tomat and A. Rigo, *ibid.* **6** (1976) 257.
[3] *Idem, ibid.* **9** (1979) 301.
[4] *Idem, ibid.* **14** (1984) 1.
[5] *Idem, ibid.* **10** (1979) 549.
[6] C. Walling, *Accounts Chem. Res.* **8** (1975) 125.
[7] J. F. Word and L. S. Myers, *Radiation Res.* **26** (1965) 483.
[8] K. R. Darnall, R. Atkinson and J. N. Pitts, Jr, *J. Phys. Chem.* **82** (1978) 1581.
[9] A. C. Lloyd, K. R. Darnall, A. M. Winer and J. N. Pitts, Jr, *ibid.* **80** (1976) 789.
[10] D. C. Nonhebel and J. C. Walton, in 'Free Radical Chemistry', (Cambridge University Press, Cambridge, 1974) Chap. 6, p. 128.
[11] C. Walling, G. M. El-Taliawi and R. A. Johnson, *J. Amer. Chem. Soc.* **96** (1974) 133.
[12] N. R. Greiner, *J. Chem. Phys.* **46** (1967) 3389.
[13] *Idem, ibid.* **53** (1970) 1070.
[14] G. E. Adams and R. L. Willson, *Trans. Faraday Soc.* **65** (1969) 2981.
[15] D. Suryanarayana, W. Chamul and L. Kevan, *J. Phys. Chem.* **86** (1982) 4822.
[16] M. N. Schuchmann and C. von Sonntag, *ibid.* **86** (1982) 1995.
[17] E. Bothe and D. Schulte-Frohlinde, *Z. Naturforsch. B* **33** (1978) 786.
[18] M. N. Schuchmann and C. von Sonntag, *J. Phys. Chem.* **83** (1979) 780.
[19] B. C. Gilbert, R. G. G. Holmes, H. A. M. Lane and R. O. C. Normal, *J. Chem. Soc. Perkin Trans.* **2** (1976) 1047.
[20] M. N. Schuchmann and C. von Sonntag, *J. Photochem.* **16** (1981) 289.
[21] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.* (1963) 3119.
[22] J. K. Kochi, *J. Amer. Chem. Soc.* **84** (1962) 2785.
[23] R. Kh. Freidlina and A. B. Terent'ev, in 'Advances in Free Radical Chemistry' Vol. 6, edited by G. H. Williams (Heyden & Son Ltd, London, 1980).