

Anodic Oxidation. Part 17.¹ The Formation of Alkyl Methyl Carbonates in the Hofer–Moest Reaction in Methanol

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The liquid products from the electrolysis of sodium butanoate in methanol containing methyl sodium carbonate at a graphite anode include propyl and 1-methylethyl methyl carbonates. 1,1-Dimethylethyl methyl carbonate is amongst the liquid products from the electrolysis of sodium 2,2-dimethylpropanoate in methanol at a platinum anode in the presence or absence of methyl sodium carbonate. Typical secondary products derived from propene or 2-methylpropene are also present in the liquid products from each of these electrolyses.

WE have shown earlier^{2,3} that the electrolysis of alkenes in methanol can lead to the formation of methyl carbonates, and that such products can be formed when the supporting electrolyte is sodium methoxide as well as sodium methyl carbonate. The results were rationalised mechanistically in terms of an initial one-electron oxidation of the alkene coupled with nucleophilic attack on the incipient radical cation by the methyl carbonate anion, either initially present, or formed during the electrolysis by oxidation of the solvent. It occurred to us that methyl carbonates might also be produced in other cases in which a cation is generated by an electrochemical oxidation in methanol, and this led us to investigate the liquid products formed by the two-electron oxidative decarboxylation of sodium carboxylates, the Hofer–Moest reaction, in methanol. To the best of our knowledge organic carbonates have not been reported as constituents of any Hofer–Moest reaction mixtures.

Since the two-electron oxidation of primary carboxylates is favoured over the one-electron Kolbe process by the use of soft graphite electrodes,⁴ we investigated the liquid products, formed in very low yield, from the constant current electrolysis at a soft graphite anode of sodium butanoate in methanol containing methyl sodium carbonate. Sodium butanoate has been electrolysed several times in methanol as part of a crossed-Kolbe reaction,^{4,5} but any Hofer–Moest products were not investigated. In view of the complexity of the product mixture, as revealed by analytical gas liquid chromatography (g.l.c.), we chose to identify some of the constituents by a detailed comparison of their behaviour on g.l.c. with that of compounds which on mechanistic grounds were thought to be likely constituents. On the basis of peak enhancement studies we consider that the compounds (1)–(8) listed in Table 1, which showed retention times identical with those of authentic samples, under three different sets of conditions (A, B, and C) are amongst those present in the product mixture. Allyl methyl carbonate (t_R 9.5 min under conditions A) was not apparently present. The formation of four of the products (1)–(4) can be rationalised in terms of attack by butanoate or methyl carbonate anion on the propyl cation (or protonated cyclopropane⁶) or the rearranged 1-methylethyl cation. Products (3) and (4) have been reported previously as products from electrolyses of

alkali-metal butanoates in water.⁷ 1- and 2-Methoxypropane, though expected products, would not have been isolated because of the work-up procedure we used. The production of alkyl methyl carbonates, propyl and 1-methylethyl methyl carbonates, (1) and (2), in the Hofer–Moest reaction is thus demonstrated for the first time. The other products (5)–(8) are secondary products derived from propene, and their formation can be rationalised mechanistically in the same way as were the structurally similar alkene-derived products reported earlier.^{2,3}

TABLE 1

Liquid products from the electrolysis of sodium butanoate in methanol containing methyl sodium carbonate at a soft graphite anode

No.	Compound	G.l.c. retention times (t_R) in min under particular conditions ^a		
		A	B	C
(1)	MeO·CO·OCH ₂ CH ₂ Me	4.7	4.1	4.2
(2)	MeO·CO·OCHMe ₂	4.6	3.0	3.5(5)
(3)	MeCH ₂ ·CH ₂ ·CO·O·CH ₂ CH ₂ Me	5.5	4.0	5.0
(4)	MeCH ₂ ·CH ₂ ·CO·O·CHMe ₂	4.5	3.0	3.3
(5)	MeO·CH ₂ ·CH(OMe)·Me	2.5	1.8	2.4
(6)	MeO·CO·O·CH(Me)CH ₂ OMe	11.5	9.8	8.7
(7)	MeO·CO·O·CH ₂ CH(OMe)Me	12.0	10.0	9.8
(8)	4-Methyl-1,3-dioxolan-2-one	21.5	18.0	16.4

^a For g.l.c. conditions A, B, and C see Experimental section.

Tertiary carboxylic acids form cation-derived products even when electrolysed at a platinum anode⁴ and so we investigated the liquid products from the electrolysis of 2,2-dimethylpropanoic acid in methanol at a platinum anode under several conditions. This acid has not apparently been electrolysed in methanol previously, but products derived from the 1,1-dimethylethyl cation have been reported for electrolyses in cyanomethane⁸ and cyanobenzene.⁹ In all our electrolyses very low yields of liquid products were formed, and the complexity of the product mixtures was again apparent from analytical g.l.c. The proportions of the minor products varied with the conditions. We did not investigate these variations systematically but made use of the variation to select mixtures for preparative g.l.c. from which certain of the products could successfully be isolated (Table 2). In addition to the six products isolated, peak enhancement studies using two different conditions for g.l.c. (A and C) pointed to the presence of methallyl

alcohol (t_R 5.3 min, condition A, Table 2). Products (9), (10), and (11) were identified by comparison with authentic samples {peak enhancement on g.l.c. [for (9) and (10)]; 1H n.m.r., i.r., and mass spectra [for (9)—(11)]}; the identity of products (12) and (13) was deduced from their spectroscopic properties (1H n.m.r. and i.r., and [for (12)] mass spectra). The hitherto unreported carbonates (10) and (11) were prepared from the corresponding alcohols by the standard method, described in the Experimental section. The results again show the

TABLE 2

Liquid products isolated by preparative g.l.c. from the electrolysis of sodium 2,2-dimethylpropanoate

No.	Compound	Electrolysis conditions ^a	t_R (A) min. ^a
(9)	MeO·CO·OCMe ₃	(c)	3.5
(10)	MeO·CO·OCH ₂ CMe=CH ₂	(a)	5.7
(11)	MeO·CO·O·CH ₂ ·CMe ₂ OMe	(a)	9.0
(12)	4,4-Dimethyl-1,3-dioxolan-2-one	(b)	17.0
(13)	MeO·CH ₂ ·CMe ₂ OMe	(c)	7.5

^a For details see Experimental section.

formation of an alkyl methyl carbonate, 1,1-dimethylethyl methyl carbonate (9) in a Hofer-Moest reaction in methanol. Peak enhancement studies using two different conditions showed that (9) was produced whether the supporting electrolyte was sodium butanoate [runs (a) and (c)] or methyl sodium carbonate [run (b)]. The other products (10)—(13) are expected secondary products from 2-methylpropene, and their formation can be rationalised mechanistically in the manner adopted earlier.^{2,3}

EXPERIMENTAL

1H N.m.r. spectra were determined on a Varian HA 100 spectrometer for CCl₄ solutions with Me₄Si as internal standard. I.r. spectra were measured in CCl₄ solution on a Perkin-Elmer 457 spectrophotometer. Mass spectra were obtained on an AEI MS-12 instrument.

Gas Chromatography.—Analytical g.l.c. was carried out on a Perkin-Elmer F 11 instrument, fitted with a flame ionisation detector, using glass columns 3 mm in internal diameter and 6 ft in length under one of the following sets of conditions (stationary phase; support, temperature): A, 5% FFAP (free fatty acid phase) on 80—100 mesh Chromosorb G, 60—220 °C at 6° min⁻¹; B, 15% PEGA (polyethylene glycol adipate) on 80—100 mesh Chromosorb W, 60—190 °C at 6 °C min⁻¹; C, 15% Harflex 370 (polypropylene glycol sebacate) on 80—100 mesh Chromosorb W, 60—220 °C at 6 °C min⁻¹. Preparative g.l.c. was carried out on a Pye 105 instrument fitted with a flame ionisation detector and a 100:1 splitter, using glass columns 3/8 in in internal diameter, under one of the following sets of conditions (stationary phase, support, column length) at the temperatures quoted: D, 7% FFAP on 60—80 mesh Chromosorb G (7 ft); E, 3% Carbowax 20 M on 60—85 mesh Chromosorb W (10 ft); F, 15% PEGA on 60—80 mesh Chromosorb W (10 ft). In all cases the carrier gas was N₂, with flow rates of ca. 35 ml min⁻¹ (F 11) and ca. 120 ml min⁻¹ (Pye 105), and the injection temperature 280 °C.

Starting Materials.—1-Methoxypropan-2-ol was isolated by preparative g.l.c. (D, isothermal, 75 °C) from the products from the base-catalysed methanolysis of methyl-

oxiran¹⁰ and had δ 1.05 (3 H, d, MeCH), 2.47 (1 H, s, OH), 3.16 (2 H, m, CH₂), 3.32 (3 H, s, OMe), and 3.78 (1 H, m, CH). Acid-catalysed methanolysis of methyloxiran¹¹ gave a mixture of 1-methoxypropan-2-ol [peak enhancement with the sample above; t_R (A) 9.7 min] and 2-methoxypropan-1-ol [t_R (A) (8.0 min) in a 1:1 ratio]. Acid-catalysed methanolysis of 1,1-dimethyloxiran¹² gave a fraction, b.p. 130—140 °C (lit.¹² 140—141 °C) containing only one major component, 2-methoxy-2-methylpropan-1-ol¹² [t_R (A) 7.0 min]. Propyl chloroformate and 1-methylethyl chloroformate were prepared by literature procedures¹³ from phosgene and the corresponding alcohols and were used without further purification.

Reference Compounds.—4-Methyl-1,3-dioxolan-2-one [t_R (A) 21.5 min] was a commercial sample; propyl butanoate [t_R (A) 5.5 min] and 1-methylethyl butanoate [t_R (A) 4.5 min] were obtained from commercial samples by preparative g.l.c. (D; isothermal 75 and 70 °C respectively). 1,2-Dimethoxypropane was isolated by preparative g.l.c. (E; isothermal 85 °C) from material b.p. 96—98 °C (lit.¹⁴ 92 °C) obtained by the methylation (NaH, Me₂SO₄) of propane-1,2-diol, and had ν_{max} 2 980, 2 920, 2 880, 2 820, 1 450, 1 370, 1 110, and 960 cm⁻¹; δ 1.06 (3 H, d, MeCH), 3.26 (2 H, d, CH₂OMe), 3.27 (6 H, s, 2 × OMe), and 3.08—3.40 (1 H, m-CH); m/e 104 (M^+) and 89 (M^+ -Me). 1,1-Dimethylethyl methyl carbonate, b.p. 127—131 °C (lit.¹⁵ 125—129 °C), ν_{max} 2 970 and 1 737 cm⁻¹; δ 1.41 (9 H, s, Me₃C) and 3.58 (3 H, s, OMe); m/e 117 (M^+ - Me), 73 (M^+ - CO₂Me), and 57 (M^+ - OCO₂Me) and allyl methyl carbonate, purified by preparative g.l.c. (D, isothermal, 75 °C) were prepared by literature methods.^{15,16} Methyl propyl carbonate¹⁶ [98% pure by g.l.c. (A)], ν_{max} 1 749 cm⁻¹; δ 0.97 (3 H, t, MeCH₂), 1.67 (2 H, m, MeCH₂), 3.69 (3 H, s, OMe), and 4.02 (2 H, m, OCH₂) and methyl 1-methylethyl carbonate¹⁶ [99% pure by g.l.c. (A)], ν_{max} 1 750 cm⁻¹, δ 1.25 (6 H, d, CHMe₂), 3.65 (3 H, s, OMe), and 4.77 (1 H, m, CHMe₂) were prepared from methanol and the corresponding alkyl chloroformate, in the presence of pyridine.¹³ *Methallyl methyl carbonate* was prepared from methallyl alcohol and methyl chloroformate, in the presence of pyridine¹³ and had b.p. 120 °C, ν_{max} 2 950, 1 750, 1 440, and 1 270 cm⁻¹; δ 1.75 (3 H, s, Me), 3.73 (3 H, s, OMe), 4.45 (2 H, s, CH₂O), and 4.87 and 4.96 (each 1 H, s, C=CH₂) (Found: C, 55.4; H, 7.9. C₆H₁₀O₃ requires C, 55.4; H, 7.7%). Similarly prepared were *methyl 2-methoxy-2-methylpropyl carbonate*, purified by preparative g.l.c. (E; 100—220 °C at 4 °C min⁻¹), ν_{max} 2 982, 1 748, 1 438, and 1 270 cm⁻¹; δ 1.16 (6 H, s, Me₂C) 3.15 (3 H, s, Me₂CO-Me), 3.69 s, OCO₂Me) and 3.89 (2 H, s, CH₂); m/e 147 (M^+ - Me), 131 (M^+ - OMe), 87 (M^+ - OCO₂Me), and 57 (M^+ - CH₂OCO₂Me) (Found: C, 51.4; H, 8.6. C₇H₁₄O₄ requires C, 51.8; H, 8.6%) and *2-methoxy-1-methylethyl methyl carbonate*, b.p. 162—164 °C, purified by preparative g.l.c. (F; isothermal 135 °C), ν_{max} 1 750 and 1 270 cm⁻¹; δ 1.25 (3 H, d, MeCH), 3.31 (3 H, s, CH₂OMe) 3.34 (2 H, m, CH₂OMe), 3.69 (3 H, s, OCO₂Me) and 4.78 (1 H, m, CH) (Found: C, 48.4; H, 7.9. C₈H₁₂O₄ requires C, 48.7; H, 8.1%). 2-Methoxy-1-methylethyl methyl carbonate [peak enhancement with the sample above, t_R (C) 8.7 min] was also obtained from the reaction of methyl chloroformate with a 1:1 mixture of 1-methoxypropan-2-ol and 2-methoxypropan-1-ol (see above) in the presence of pyridine,¹³ which gave as the other product *2-methoxypropyl methyl carbonate* [t_R (C) 9.8 min], which was isolated by preparative g.l.c. (F; isothermal 135 °C) (Found: C, 48.7; H, 8.3%).

Electrolysis of Butanoic Acid.—Butanoic acid (8.81 g, 0.1

mol) was added to sodium methoxide [from sodium (2.3 g, 0.1 g-atom) in dry methanol (200 ml)]. Methyl sodium carbonate (9.8 g, 0.1 mol) was added and the mixture was electrolysed using a soft graphite anode (British Acheson Electrodes Ltd., grade AGLR) at a constant current of 0.5 A and a voltage of 9.5–21 V for 48 h in the cell previously described.¹⁸ The mixture was then filtered, and the filtrate was concentrated, to reduce the volume by a half, diluted with water (300 ml), and extracted with ether (4 × 150 ml). The combined ethereal extracts were washed with water (150 ml), 10% aqueous sodium hydrogen carbonate (150 ml), and water (150 ml), dried, (MgSO₄), and the solvent distilled, to yield a yellow oil (0.5 g). The material was analysed by g.l.c. under conditions A, B, and C, with the results shown in Table 1. Correspondence in retention times was demonstrated in every case by the technique of peak enhancement.

Electrolyses of 2,2-Dimethylpropanoic Acid.—(a) 2,2-Dimethylpropanoic acid (10.2 g, 0.1 mol) was added to methanolic sodium methoxide [from sodium (2.3 g, 0.1 g-atom) in dry methanol (250 ml)] and the mixture was electrolysed using a platinum anode and a mercury pool cathode in the cell described previously¹⁹ at an initial current of 2.5 A at 100 V. After 6.5 h the current had fallen to a steady value of 0.5 A. The mercury was changed three times during the electrolysis. (b) Carbon dioxide was bubbled through methanolic sodium methoxide [from sodium (4.6 g, 0.2 g-atom) and dry methanol (200 ml)] to produce a suspension of methyl sodium carbonate. 2,2-Dimethylpropanoic acid (10.2 g, 0.1 mol) was added to the mixture, and the resulting suspension was then electrolysed at a constant current of 0.5 A for 48 h in the simple undivided cell with platinum electrodes described previously.² (c) 2,2-Dimethylpropanoic acid (10.2 g, 0.1 mol) was added to methanolic sodium methoxide [from sodium (0.46 g, 0.02 g-atom) and dry methanol (200 ml)] and the resulting solution was electrolysed at a constant current of 0.5 A for 48 h in the simple undivided cell used in (b).²

In each case the methanolic solution (from which any solid had been filtered off at the end of the electrolysis) was concentrated by the distillation of methanol (150 ml). The residue was treated with water (250 ml) and ether (150 ml), and the mixture equilibrated. The layers were separated, and the aqueous layer was extracted further (3 × 100 ml) with ether. The combined ethereal solutions were washed with 10% aqueous sodium hydrogen carbonate, and dried (MgSO₄), and the ether was distilled. The oily product mixtures [(a) 0.5 g; (b) 1.50 g; (c) 1.25 g] were then examined by analytical g.l.c. under conditions A. 1,1-Dimethylethyl methyl carbonate (9) was isolated from mixture (c) by preparative g.l.c. (D; 60–220 °C at 3 °C min⁻¹) and shown to be identical with an authentic sample spectroscopically (¹H n.m.r., i.r., and mass spectra); peak en-

hancement studies under conditions A and C also showed that (g) was present in mixtures (a) and (b). Of the other products listed in Table 2, 2-methoxy-2-methylpropyl methyl carbonate (11) and methallyl methyl carbonate (10) were isolated from mixture (a) by preparative g.l.c. (E; 60–220 °C at 6° min⁻¹) and shown to be identical with authentic samples spectroscopically (¹H n.m.r., i.r., and mass spectra) whilst 4,4-dimethyl-1,3-dioxolan-2-one²⁰ (12), ν_{\max} 2 970, 1 830, 1 811, and 1 275 cm⁻¹; δ 1.50 (6 H, s, Me₂C) and 4.07 (2 H, s, CH₂) and 1,2-dimethoxy-2-methylpropane²¹ (13), ν_{\max} 2 964, 1 436, 1 122, and 1 032 cm⁻¹; δ 1.32 (6 H, s, Me₂C), 3.25 (6 H, s, 2 × OMe), and 3.68 (2 H, s, CH₂) were isolated by preparative g.l.c. from (b) (D; 60–220 °C at 4 °C min⁻¹) and (c) (D; 60–220 °C at 3 °C min⁻¹) respectively and could be identified spectroscopically (¹H n.m.r., i.r.).

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