D–H Exchange and Hydroxylation of ($^2H_3$)Acetic Acid in Aqueous Solution during Glow Discharge Electrolysis

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Glow discharge electrolysis of CD_3CO_2H in 0.006 M NaCl solution and also in carbonate-free distilled water simultaneously gives rise to both $HOCD_2CO_2H$ and CD_2HCO_2H, indicating the coupling of OH and H radicals with the CD_2CO_2H radical intermediate.

Glow discharge electrolysis (G.D.E.) is a type of chemical change due to the glow discharge between a conducting solution and an electrode in contact with the solution. Hickling[1] has assumed that the G.D.E.-promoted reaction is mainly initiated by OH and H radicals which arise from the decomposition of water molecules caused by bombardment of gaseous ions generated in the discharge zone. However, there is as yet no concrete evidence for the intervention of OH and H radicals in the reaction of organic materials.

We now report strong evidence that both OH and H radicals play a crucial role in the G.D.E.-promoted reaction of CD_3CO_2H in aqueous solution.

The sample solution (80 ml) was prepared by mixing CD_3CO_2D (99.8%, 100 mg) with NaCl solution (0.006 M) or carbonate-free distilled water (in the latter case discharge against the low conductance solution was unstable, so usually the supporting electrolyte was used). Two types of electrolysis cells[1,2] were used; a single straight tube (S-cell) and a U-shaped tube (U-cell). In the U-cell, the anode and cathode compartments were separated by a fine porosity glass frit and G.D.E. was carried out in the anodic compartment. The anode was a platinum wire and the cathode was a coil of platinum wire. They were always arranged so that the cathode was completely immersed in the solution and the anode was fixed so as to be in contact with the liquid surface. G.D.E. was carried out at 30(±2) °C with saturation by argon and with constant stirring. The applied electric current was 75 mA at 900—1100 V.

After G.D.E., the reaction mixture was neutralized with NaOH, evaporated to dryness under reduced pressure, esterified with diazomethane (DAM), and examined by g.l.c. (Figure 1). Peak 2 was assigned to $HOCD_2CO_2Me$ by mass

Table 1. Results for G.D.E. of CD_3CO_2H in distilled water and 0.006 M NaCl solution using S- and U-cells.[a,b]

	S-cell			U-cell							
	G.D.E.			G.D.E.				Electrolysis[c]			
Time/min	10	(10)[d]	40	30		90		30		90	
Current/mA	75	(75)	75	75		75		75		75	
Voltage/V	900	(900)	900	1100		1100		600		600	
				anode	cathode	anode	cathode	anode	cathode	anode	cathode
CD_3CO_2H/mM	18.3	(19.1)	13.2	16.6	20.0	13.6	15.9	20.2	19.6	23.3	16.6
CD_2HCO_2H/mM	0.71	(0.20)	0.62	0.73	—	0.61	—	—	—	—	—
$HOCD_2CO_2H$/mM	2.0	(0.56)	4.6	2.6	—	3.5	—	—	—	—	—
% Released carbon	0.0	(0.0)	7.5	0.0[e]		15.1[e]		0.0[e]		0.0[e]	

[a] Results of G.D.E. in distilled water are shown in parentheses. [b] Initial substrate concentration 20 mM. [c] Control experiment. [d] Discharge did not proceed continuously. [e] Determined for whole sample obtained from anode and cathode compartments.

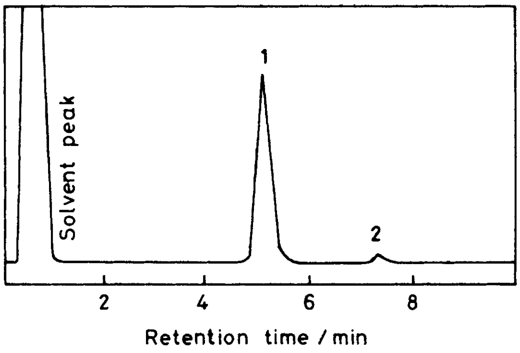

Figure 1. G.l.c. of the DAM-treated reaction mixture obtained by G.D.E. of CD_3CO_2H in the S-cell for 40 min. G.l.c. conditions: column PEG-20M, detector TCD, column temp 50 °C, carrier gas He.

spectroscopy [m/z 92 (M^+, 4%), 33 (27), 43 (56), 45 (50), and 56 (100)]. Peak 1 [m/z 46 (100%), 45 (11), and 44 (4)] was identified as arising from a mixture of CD_3CO_2Me and CD_2HCO_2Me by the fact that the relative intensity at m/z 45 (CD_2HCO^+)† is evidently different from that for CD_3CO_2Me [m/z 46 (100%), 45 (8), and 44 (4)], whereas there is no marked difference in the intensities at m/z 44 (CDH_2CO^+) between the spectrum for peak 1 and CD_3CO_2Me. Thus, these results indicate that D–H exchange of CD_3CO_2H by G.D.E. gives rise to CD_2HCO_2H but not to CDH_2CO_2H.

Table 1 shows the results of G.D.E. for CD_3CO_2H in the S- and U-cells. The concentrations of CD_3CO_2H and CD_2HCO_2H were estimated by h.p.l.c. and ^1H n.m.r. spectroscopy. The released carbon‡ was determined by a total organic carbon analyser. It is apparent that both $HOCD_2CO_2H$ and CHD_2CO_2H are formed by G.D.E. of CD_3CO_2H not only in 0.006 M NaCl solution but also in carbonate-free distilled water. In contrast with G.D.E., electrolysis does not lead to any chemical change other than the migration of the substrate from the cathode to the anode. These results indicate that D–H exchange and hydroxylation of CD_3CO_2H take place simultaneously during the course of G.D.E., regardless of the presence or absence of the supporting electrolyte. A possible radical mechanism is shown in equation (1). The G.D.E.-promoted reaction is initiated by abstraction of deuterium from the substrate with OH and/or H radicals to generate the CD_2CO_2H radical, which then combines competitively with H and OH radicals yielding HCD_2CO_2H and $HOCD_2CO_2H$. According to the proposed mechanism, the initial deuterium abstraction must be the rate-determining process. This is in accordance with the fact that the first-order rate constant (k_D 1.1×10^{-2} min^{-1}) for the disappearance of CD_3CO_2H was found to be much smaller than that (k_H 2.0×10^{-2} min^{-1}) for CH_3CO_2H.§

$$\left.\begin{array}{c} CD_3CO_2H \\ + \\ \cdot OH \text{ and } \cdot H \end{array}\right\} \rightarrow \begin{array}{c} HOCD_2CO_2H \\ \uparrow \cdot OH \\ \cdot CD_2CO_2H \\ \downarrow \cdot H \\ HCD_2CO_2H \end{array} \qquad (1)$$

On the basis of these results, we conclude that OH and H radicals play an important role in G.D.E.-promoted reactions of organic compounds.

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References

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† The fragment with m/z 45 is not detectable for CH_3CO_2Me which is characterized by the base ion (CH_3CO^+) with m/z 43 (ref. 3).

‡ During the G.D.E., both CH_3CO_2H and $HOCH_2CO_2H$ were oxidized finally to gaseous compounds (CO and CO_2).

§ The data were obtained by G.D.E. in the S-cell: initial substrate concentration 10 mM, current 75 mA, voltage 900 V, time 0—40 min.