

## Electrochemical Syntheses. Part VII.<sup>1</sup> Isomer Distribution in the Partial Oxidation of n-Alkanes

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The electrochemical oxidation of alkanes in weak acidic solution ( $\text{CH}_2\text{Cl}_2\text{-CF}_3\cdot\text{CO}_2\text{H}$ ) was investigated. The non-statistical isomer distribution of n-decane oxidation products seems to parallel slight differences in the reactivity of the  $\text{CH}_2$  groups. A mechanism involving free carbocations is suggested.

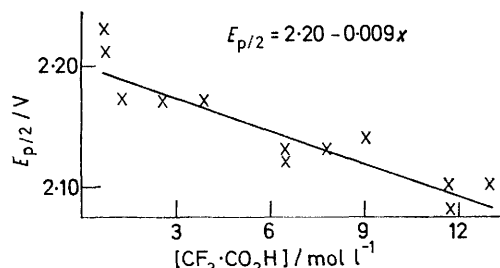
ALKANES can be oxidized both chemically, *e.g.* in solutions of cobalt(III) acetate in acetic acid with addition of a strong acid<sup>2</sup> or of lead(IV)<sup>3</sup> or cobalt(III) trifluoroacetate<sup>4</sup> in trifluoroacetic acid, and electrochemically, *e.g.* in some aprotic media,<sup>5-7</sup> in fluorosulphuric acid,<sup>8</sup> and in trifluoroacetic acid.<sup>9</sup>

In the course of synthetic work on the electrochemical oxidation of alkanes,<sup>10</sup> we recently demonstrated that the oxidation potentials of certain alkanes are lowered (to more cathodic potentials) not only in fluorosulphuric acid (a 'super acid') as compared with aprotic media, but also in the more weakly acidic solutions of, for example, fluorosulphuric acid, methanesulphonic acid, or trifluoroacetic acid in acetic acid. On the basis of electrochemical measurements we assumed the previously postulated<sup>8</sup> rapid protonation reaction to occur prior to the electrochemical reaction in the oxidation of alkanes. For our synthetic purposes it was of interest to know whether the decrease in alkane oxidation potential occurs only after protonation by very strong acids or if it is a general result of the presence of protic substances. A preliminary study of our reaction system was carried out by voltammetry at stationary platinum electrodes. Mixtures of trifluoroacetic acid, acetic acid, and dichloromethane were used as solvents.

### RESULTS AND DISCUSSION

**Voltammetry.**—Cyclic voltammetry at 'inert' † stationary platinum electrodes was applied. In  $\text{CH}_2\text{Cl}_2\text{-0.1M-(Bu}_4\text{N)PF}_6$  as well as in  $\text{CH}_2\text{Cl}_2\text{-6.5M-MeCO}_2\text{H-0.1M-(Bu}_4\text{N)PF}_6$  no oxidation peak for cyclohexane was observed. Only in the extreme potential region of solvent decomposition was it possible to measure an additional weak current due to substrate oxidation. In  $\text{MeCO}_2\text{H-4.0M-CF}_3\cdot\text{CO}_2\text{H}$  (trifluoroacetic acid is weak in acetic acid<sup>12</sup>) an additional current due

to cyclohexane oxidation again could only be detected in the extreme potential region of solvent decomposition. Different results were obtained with  $\text{CH}_2\text{Cl}_2\text{-CF}_3\cdot\text{CO}_2\text{H}$  mixtures. With increasing  $\text{CF}_3\cdot\text{CO}_2\text{H}$  concentration we observed a cathodic shift in the oxidation potential for cyclohexane (Figure). This shift might be due to a



$E_{p/2}$  vs.  $[\text{CF}_3\text{CO}_2\text{H}]$  (xM) in  $\text{CH}_2\text{Cl}_2\text{-0.1M-Bu}_4\text{NPF}_6\text{-3.7} \times 10^{-2}\text{-M-C}_6\text{H}_{12}$ ; Scan rate ( $v$ ) =  $50 \text{ mV s}^{-1}$

change in alkane activation energy<sup>13</sup> and/or to a chemical reaction following electron transfer (*i.e.* a nucleophilic reaction of the electrochemically generated species with  $\text{CF}_3\cdot\text{CO}_2\text{H}$ ). Comparing our cyclovoltammetric data with the diagnostic criteria of Nicholson, Shain, and Wopschall<sup>14-16</sup> we only found qualitative correspondence to a reversible electrochemical reaction followed by a rapid chemical reaction. Having considered the criticisms levelled at interpretations based on electroanalytical measurements<sup>17</sup> we favour a direct oxidation without change of activation energy (*e.g.* by proton assistance) and a trapping reaction by the solvent for alkane oxidation in these weakly acidic media.

**Preparative Electrolyses.**—The preparative electrolysis of cyclohexane in  $\text{CH}_2\text{Cl}_2\text{-2.5M-CF}_3\cdot\text{CO}_2\text{H}$  yielded cyclohexyl trifluoroacetate (91%) and cyclohexyl chloride (4%). The reaction in this nucleophilic medium did not lead to solvolysis products of the methylcyclopentyl

† The half-wave oxidation potentials for cyclohexane at Au, Rh, and Ir are similar to that at Pt anodes.<sup>11</sup>

<sup>1</sup> Part VI, G. Bockmair and H. P. Fritz, *Electrochim. Acta*, in the press.

<sup>2</sup> J. Hanotier, *J.C.S. Perkin II*, 1972, 2247.

<sup>3</sup> R. E. Patch, *J. Amer. Chem. Soc.*, 1967, 89, 3662.

<sup>4</sup> R. Tang and J. K. Kochi, *J. Inorg. Nuclear Chem.*, 1975, **35**, 3845.

<sup>5</sup> D. B. Clark, M. Fleischmann, and D. Pletcher, *J. Electroanalyt. Chem.*, 1973, **42**, 133.

<sup>6</sup> M. Fleischmann and D. Pletcher, *Tetrahedron Letters*, 1968, 6255.

<sup>7</sup> T. M. Siegel, L. L. Miller, and J. Y. Becker *J.C.S. Chem. Comm.*, 1974, 34.

<sup>8</sup> J. Bertram, J. P. Coleman, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 374.

<sup>9</sup> D. B. Clark, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 1578.

<sup>10</sup> H. P. Fritz and Th. Würminghausen, *J. Electroanalyt. Chem.*, 1974, **54**, 18.

<sup>11</sup> H. P. Fritz and Th. Würminghausen, unpublished results.

<sup>12</sup> B. M. Rode, A. Engelbrecht, and J. Schantl, *Z. Phys. Chem.*, 1973, **253**, 1/2, 17.

<sup>13</sup> K. J. Vetter, 'Elektrochemische Kinetik,' Springer-Verlag, Berlin, 1961.

<sup>14</sup> R. H. Wopschall and I. Shain, *Analyt. Chem.*, 1967, **39**, 1514.

<sup>15</sup> R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 707.

<sup>16</sup> S. Piekarski and R. N. Adams, 'Physical Methods of Chemistry,' Part Iia, eds. Weissberger and Rossiter, Wiley-Interscience, New York, 1971, p. 556.

<sup>17</sup> R. N. Adams, 'Electrochemistry at Solid Electrodes,' Dekker, New York, 1969, p. 255.

ion, which according to Olah *et al.* and Fleischmann *et al.*,<sup>8</sup> is more stable in 'super acids' than the cyclohexyl ion.

Preparative electrolyses of n-decane (which is more difficult to oxidise than cyclohexane) were performed in the systems  $\text{CH}_2\text{Cl}_2$ -6.5M- $\text{CF}_3\cdot\text{CO}_2\text{H}$ -0.05M- $(\text{Bu}_4\text{N})\text{PF}_6$  and  $\text{MeCO}_2\text{H}$ -4M- $\text{CF}_3\cdot\text{CO}_2\text{H}$ -1M- $\text{MeCO}_2\text{Na}$ . In the first system we obtained isomeric trifluoroacetoxy-n-decanes (68%) with a current yield of 36%, bistrifluoroacetoxy-n-decanes (11%), and non-distillable, highly viscous products (21%) after reaction of 90% of the n-decane. Neither olefins nor rearrangement products (secondary to tertiary) were detected. The trifluoroacetoxy-n-decane isomer distribution is given in the Table (a). The isomer ratios varied by less than 2% during the electrolysis. In the second system [Table (b)] we

and found an isomer distribution [Table (d)] similar to our other results. A change from divided to undivided cells did not affect the oxidation products.

The change from n-octane to n-decane should not be responsible for the observed drastic change in isomer distribution. From the work of Asinger *et al.*,<sup>18</sup> on alkane radical reactions (showing statistical isomer distributions) it is known that the finding of a non-statistical isomer ratio can be due to systematic errors in the analytical work-up of products. We therefore took special care not to introduce any 'artificial' alteration of the experimental isomer distribution. The electrolyte-product mixtures were analysed by g.l.c. either directly or after extraction of the esters with ether, and the results were checked against a mixture of authentic trifluoroacetoxy-n-decanes. The results did

Isomer distribution of n-decane oxidation products (mono-acetoxy- or -trifluoroacetoxy-n-decanes)

	Isomer:	1-	2-	3-	4-	5-
(a)	Trifluoroacetates <sup>a</sup> Standard devn. ( $m = 14$ ) Rel. $t_R$ <sup>b,c</sup>	4.66	14 0.3 3.10	22 0.3 2.72	28 0.3 2.41	36 0.4 2.28
(b)	Trifluoroacetates <sup>a</sup> Acetates <sup>d</sup> Rel. $t_R$ of acetates <sup>b</sup>	6.38	17 16 4.81	22 18 4.16	28 29 3.76	33 37 3.58
(c)	Trifluoroacetates <sup>a</sup>		15	22	27	36
(d)	Trifluoroacetates <sup>a</sup>		16	23	27	34
(e)	Calc. rel. % <sup>e</sup>	2	8	20	32	38
(f)	RH <sup>+</sup> - RH charge difference	0.7	13.4	20.8	29.7	35.4

<sup>a</sup> Rel. yields (g.l.c.) (%). <sup>b</sup> With respect to n-decane (rel.  $t_R$  1.00). <sup>c</sup> Column of di-n-decyl phthalate. <sup>d</sup> Column of Apiezon  
<sup>e</sup> From ref. 23. <sup>f</sup> From ref. 25.

obtained acetoxy- and trifluoroacetoxy-n-decanes in the ratio 1.8 : 1 (the molar ratio of the acids was 3.3 : 1) and with a similar isomer distribution.

The result of the electrochemical oxidation of n-octane at platinum electrodes in  $\text{CF}_3\cdot\text{CO}_2\text{H}$ -0.4M- $(\text{Bu}_4\text{N})\text{BF}_4$ <sup>9</sup> is in contrast to the isomer distribution found by us with n-decane: from the previous experiment a strictly statistical ratio of the isomeric 2-, 3-, and 4-trifluoroacetoxy-n-octanes is reported, whereas we obtained the non-statistical isomer distribution shown in the Table (c) after controlled potential electrolysis of n-decane in  $\text{CF}_3\cdot\text{CO}_2\text{H}$ -0.05M- $(\text{Bu}_4\text{N})\text{PF}_6$ . We considered that this discrepancy might be ascribed to the *ca.* ten-fold supporting electrolyte concentration used by Fleischmann *et al.*;<sup>9</sup> in that experiment the Helmholtz double layer could mainly be built up by aprotic alkyl groups and so a different reaction path might be induced. We therefore tested a solution in  $\text{CF}_3\cdot\text{CO}_2\text{H}$ -0.4M- $(\text{Bu}_4\text{N})\text{PF}_6$

\* Studies of rearrangement products in the anodic oxidation of branched alkanes strongly hint at 'free' carbocation intermediates.<sup>20</sup>

<sup>18</sup> F. Asinger and K. Halcour, *Chem. Ber.*, 1961, **94**, 83, and references cited there.

<sup>19</sup> J. T. Keating and P. S. Skell, 'Carbonium Ions,' vol. II, eds. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1970.

not change during g.l.c. analysis, nor was the isomer distribution altered in pure trifluoroacetic acid, in which acid-catalysed solvolysis might occur. We therefore postulate that this non-statistical isomer distribution is not due to a radical reaction path and that the number of electrons transferred ( $n$ ) is two.<sup>9</sup>

In view of the general observation that the weakest bond in a molecule is most readily oxidised, it can be understood why no 1-isomer is obtained. As it is unlikely that a given methylene group of an alkane chain is preferentially orientated towards the electrode, the isomer distribution should be directly representative of the electronic structure of the intermediate carbocation, which should be 'hot' or 'free'<sup>19,\*</sup> rather than 'encumbered'<sup>21</sup> in view of its mode of formation. From the concept of inductive effects<sup>22</sup> one would expect the probability of finding a positively charged carbon atom to increase towards the centre of the molecule. The net positive charge distribution in the carbon skeleton of an n-decane radical cation has been calculated by

<sup>20</sup> H. P. Fritz and Th. Würminghausen, unpublished results.

<sup>21</sup> H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, **20**, 496.

<sup>22</sup> See *e.g.* calculations of S. Fliszar *et al.*, *J. Amer. Chem. Soc.*, 1972, **94**, 1068; 1974, **96**, 4352, 4358.

Lorquet.<sup>23</sup> Assuming a similar relative charge distribution for  $R^+$ , we estimate the relative isomer distribution of the products of reactions of such ions with a nucleophile to be as in the Table (e). The C-H bond charge density was calculated to be significant only at position 2. This would presumably lead to an increase in the percentage of the 2-isomer. In the light of these numerical values the similarity of the experimental and the estimated isomer distributions is reasonable.<sup>24</sup>

A recent INDO calculation on n-decane<sup>25</sup> yielded the values given in the Table (f) for the differences in charge density between the ion and the neutral molecule. An isomer distribution similar to our experimental one would be expected from this set of data.

'Free carbocation' reaction products obtained after deamination of n-octylamine or 1-propylpentylamine<sup>21</sup> or after decarboxylation of lauric acid<sup>19</sup> were to a great extent the isomer with the functional group at the same carbon atom. In direct hydrocarbon oxidation, as here, the isomer distribution is not influenced by a leaving group. In addition it is not necessary that the most stable carbocation be formed *via* rearrangement before 'trapping,'\* although the possibility of hydride shifts cannot be excluded.

The isomer distribution of trifluoroacetoxy-n-decanes after oxidation of n-decane with  $\text{Et}_3\text{NO}(\text{Et}_2\text{NOH})\text{Fe}^{\text{II}}$  in  $\text{CF}_3\cdot\text{CO}_2\text{H}$  found by Deno and Pohl<sup>26</sup> differs from our results, although these authors also suggest a reaction path *via* carbocations ('encumbered' in this case). Additional experiments are in progress to answer the remaining questions.

#### EXPERIMENTAL

The cyclic voltammetry cell and the apparatus have been described elsewhere.<sup>10</sup> For electroanalyses a silver- $10^{-2}\text{M}$ -silver trifluoroacetate reference electrode in dichloromethane-6.5M-trifluoroacetic acid-0.1M-tetrabutylammonium hexafluorophosphate separated by a D4 sinter was used. During measurements with dichloromethane-trifluoroacetic acid the reference electrode was separated from the bulk solution by a dichloromethane-6.5M-trifluoroacetic acid-1M-tetrabutylammonium hexafluorophosphate bridge (D4).<sup>27</sup> The potential of two identical reference electrodes in the various electrolytes was found to differ by less than 3 mV. The potential drop due to resistance was shown to be negligible by measuring with a Tacussel CDCO instrument. For the cyclohexane oxidation the standard deviation of 10  $E_{p/2}$  measurements in dichloromethane-7.8M-trifluoroacetic acid-0.1M-tetrabutylammonium hexafluorophosphate was calculated to be 13 mV.

For preparative work a Teflon cell with two 98 cm<sup>2</sup> platinum electrodes 1.7 mm apart and with a Normag glass-Teflon pump for forcing convection was employed.

\*  $k_{\text{rearr.}}/k_{\text{tr.}}$  ca. 3 for the deoxidation of butan-2-ol (ref. 19, p. 580).

<sup>23</sup> J. Lorquet, 'Theory of Mass Spectrometry,' vol. 3, ed. W. L. Mead, Elsevier, Amsterdam, 1966.

<sup>24</sup> See, however, R. Hoffmann, *J. Chem. Phys.*, 1964, **40**, 2480.

<sup>25</sup> L. Ebersson, personal communication.

<sup>26</sup> N. C. Deno and D. G. Pohl, *J. Amer. Chem. Soc.*, 1974, **95**, 6680.

The potential of the working electrode was measured from the rear of the electrode<sup>28</sup> with saturated calomel electrode (s.c.e.), separated from the electrolyte by a D4 glass frit. Products were analysed by i.r. spectroscopy (Beckmann IR10 instrument), quantitative %C and %H determinations, and comparison of g.l.c. retention times with those of authentic samples on two different columns. The g.l.c. analyses were carried out on a Perkin-Elmer 116 E instrument with a thermal conductivity detector and columns of di-n-decyl phthalate on Chromosorb B or Apiezon M on Celite 545 at 160 °C. Flow rates were 46 ml min<sup>-1</sup>.

*Reagents and G.l.c. Standards.*—Trifluoroacetic acid (Roth) was distilled prior to use. Methylene chloride (Riedel-De Haen) was dried ( $\text{P}_4\text{O}_{10}$ ), distilled, and purified chromatographically on alumina. Tetra-n-butylammonium hexafluorophosphate was precipitated from water by mixing aqueous tetra-n-butylammonium hydroxide (Fluka) and hexafluorophosphoric acid (Merck), filtered off, recrystallised from ethyl alcohol, and dried in high vacuum at 140 °C for 24 h. The trifluoroacetate standards were prepared by mixing equimolar amounts of the corresponding alcohols and trifluoroacetic acid anhydride.<sup>29</sup> After distillation the trifluoroacetates were gas chromatographically pure. The absence of total rearrangement on esterification was tested by <sup>1</sup>H n.m.r. spectroscopy of the 1- and 2-trifluoroacetoxy-n-decanes. They showed a triplet or a sextet, respectively, for the proton(s) adjacent to  $\text{CF}_3\text{CO}_2$  ( $\delta$  4.3 and 5.1). The acetoxy-n-decanes were prepared with sulphuric acid and acetic acid.<sup>30</sup> The n-decane (analytical reagent) was used as supplied; cyclohexane was treated with oleum (5%) and dried with sodium prior to use. Cyclohexyl chloride standard was used as supplied. For preparative electrolyses 110 ml of solvent containing supporting electrolyte and 0.1 mole of alkane were employed.

*Cyclohexane Oxidation.*—The anode potential was pulsed for 30 s at 2.5 vs. s.c.e. and for 1 s at 0.15 V vs. s.c.e. in dichloromethane-2.5M-trifluoroacetic acid-0.05M-tetrabutylammonium hexafluorophosphate. After 50 000 C had passed and the cyclohexane had been consumed the electrolysis was terminated and the electrolyte worked up by pouring it into water, neutralizing, extracting with ether, and evaporating the extract. The residue consisted of 91% cyclohexyl trifluoroacetate and 4% cyclohexyl chloride (by g.l.c.). The products were identified by g.l.c. retention times, separately and in mixtures. Three other products (1, <1, and 3%), were not identified.

*n-Decane Oxidation.*—(i) The oxidation was carried out in dichloromethane-6.5M-trifluoroacetic acid-0.05M-tetrabutylammonium hexafluorophosphate galvanostatically at 7 mA cm<sup>-2</sup> (2.6 V vs. s.c.e. average working potential) until 90% of the n-decane had been consumed. (ii) The electrolysis was done in acetic acid-4M-trifluoroacetic acid-1M-sodium acetate. The working potential of 2.6 V vs. s.c.e. was applied for 30 s; this was followed by a 1 s pulse of 0.3 V vs. s.c.e. The oxidation was ended after the consumption of 47% n-decane. (iii) n-Decane was oxidised

<sup>27</sup> C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Non-aqueous Systems*, Dekker, New York, 1970, p. 17.

<sup>28</sup> R. Piontelli, G. Bianchi, U. Bertocci, C. Guerri, and B. Rivolta, *Z. Elektrochem.*, 1955, **59**, 778.

<sup>29</sup> A. M. Lovelace, D. A. Rausch, and W. Postelnek, 'Aliphatic Fluorine Compounds,' Reinhold, New York, 1958.

<sup>30</sup> H. Henecka, 'Methoden der Organischen Chemie, Sauerstoffverbindungen, III,' ed. Houben-Weyl, Thieme Verlag, Stuttgart, 1952.

at 2.5 V *vs.* s.c.e. for 10 s and at 0.4 V for 1 s in trifluoroacetic acid–0.05M-tetrabutylammonium hexafluorophosphate until 10 000 C had passed. (iv) The oxidation (iii) was repeated with 0.4M-tetrabutylammonium hexafluorophosphate instead of 0.05M. Product identification was carried out by direct injection of the electrolysis mixture into the gas chromatograph and comparing g.l.c. retention times separately and in mixtures. Relative yields were calculated by comparing peak areas with those of g.l.c. standards. The standard deviations of run (i) are given in the Table (a). The bistrifluoroacetoxy-n-decanes obtained were not resolved gas chromatographically. The corre-

sponding fraction from vacuum distillation showed C, 45.85; H, 5.45 (Calc. for  $C_{14}H_{20}F_6O_4$ : C, 45.9; H, 5.45%). The i.r. spectrum was typical of an alkyl trifluoroacetate (compared with authentic monotrifluoroacetoxydecane):  $\nu_{max}$  (film) 1 785s, 1 550w, 1 460m, 1 380m, 1 340m, 1 210vs, 1 160vs, 970w, 860w, 770m, and 725m  $cm^{-1}$ .

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