mp 209–209.5 °C); mass spectrum, *m/e* (relative intensity) 192.0932 (calcd for $C_{15}H_{12}$, 192.0939), (M^+, 100); ^1H NMR 8.33 (d, 2 H), 7.87 (m, 4 H), 7.38 (m, 3 H), 2.53 (s, 3 H); λ_{max} (cyclohexane) 323 nm (ϵ 110 000), 325 (1075), 342 (1790), 360 (2500), 380 (2100).

Reaction of 15a with Benzyne. The diene **15a** (0.700 g, 3.7 mmol) was added to a stirred solution of benzenediazonium-2-carboxylate (1.03 g, 7 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2. The mixture was then heated to reflux for 1 h, the solvent removed under reduced pressure, and the residue chromatographed on Al_2O_3 (eluting with petroleum ether) to give a white solid, recrystallized from methanol as **52**: 0.800 g (80%); mp 93–95 °C; mass spectrum, *m/e* (relative intensity) 264.0430 (calcd for $C_{15}H_{14}{}^{35}Cl_2$, 264.0472), 268, 266, 264 (M^+, 1:6:9, 100), 231, 229 ($M^+ - Cl$, 1:3, 60); ^1H NMR 7.00 (s, 4 H), 3.33 (m, 4 H), 1.96 (s, 6 H).

Oxidation of 52. A solution of pyridinium hydrobromide perbromide (1.78 g, 5.6 mmol) in dry THF (15 cm^3) was added dropwise to a solution of **52** (0.720 g, 2.6 mmol) in dry THF (30 cm^3) under N_2. The reaction was stirred for a further 2 h, the solution reduced to half its volume by evaporation under reduced pressure, and the remaining solution chromatographed on Al_2O_3 (eluting with petroleum ether) to give a white solid, recrystallized from methanol as **53**: 0.30 g (45%); mp 110–112 °C; mass spectrum, *m/e* (relative intensity) 266, 264, 262 (M^+, 1:6:9, 35), 229, 227 ($M^+ - Cl$, 1:3, 100); ^1H NMR 7.78 (m, 2 H), 7.44 (m, 4 H), 3.00–1.80 (m, 6 H); λ_{max} (hexane) 227 nm (ϵ 70 000), 265 (3900), 275 (4780), 284 (4780), 294 (2980). Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.44; H, 4.56; Cl, 26.99. Found: C, 68.10; H, 4.63; Cl, 26.03.

Reaction of 53 with Base. A solution of **53** (83 mg, 3.1 mmol) in dry THF (1 cm^3) was added to a stirred solution of KO-*t*-Bu (336 mg, 3 mmol) in dry THF (4 cm^3) under N_2. Stirring was continued for 3 h, and the mixture was chromatographed on Al_2O_3 (eluting with petroleum ether–CH_2Cl_2, 9:1) to give a yellow oil which was not the desired product.

Reaction of 36 with Benzyne. The diene **36** (0.510 g, 1.8 mmol) and benzenediazonium-2-carboxylate (0.450 g, 3 mmol) in dry CH_2Cl_2 (30 cm^3) were heated to reflux for 2 h. Evaporation of the solvent gave a solid residue which was recrystallized from ethanol as **54**: 0.600 g (80%); mp 178–180 °C; mass spectrum, *m/e* (relative intensity) 420, 418, 416 (M^+, 1:6:9, 100); ^1H NMR 7.40 (m, 14 H), 3.65 (s, 2 H), 3.20 (s, 4 H), 2.10 (s, 2 H).

Reaction of 54 with Base. KO-*t*-Bu (0.800 g, 7 mmol) was added to a solution of **55** (0.140 g, 0.34 mmol) in dry THF and the mixture stirred under N_2 for 90 min. Further KO-*t*-Bu (0.800 g, 7 mmol) was then added and stirring continued for a further 1 h. The mixture was filtered through Al_2O_3 (eluting with ether), the extracts were washed with water (2 × 50 cm^3) and dried (Na_2SO_4), and the solvent was removed by evaporation to give **55**: 20 mg (19%); mass spectrum, *m/e* (relative intensity) 344 (M^+, 100); ^1H NMR 8.05–7.10 (m, 17 H), 2.30 (s, 3 H).

Oxidation of 54. Bromine (0.800 g, 10 mmol) was added to a solution of **55** (1.0 g, 2.4 mmol) in CCl_4 (15 cm^3) at 0 °C, and the mixture was then warmed to 60 °C for 1.5 h. The solvent was removed under reduced pressure to give **56** (0.600 g, 60%): mass spectrum, *m/e* (relative intensity) 418, 416, 414 (M^+, 1:6:9, 100); ^1H NMR 7.65–6.85 (m, 16 H), 4.10 (m, 2 H), 2.15 (m, 2 H).

Acknowledgment. D.D. thanks the Iranian Government and M.M.M. the Science Research Council (United Kingdom) for studentships.

Registry No. 3, 57867-58-0; **4**, 65886-90-0; **5**, 4841-85-4; **6**, 57867-52-4; **7**, 57867-53-5; **8a**, 57867-54-6; **8b**, 57867-55-7; **9**, 57867-56-8; **10b**, 74663-82-4; **11**, 74725-24-9; **12**, 74725-25-0; **13a**, 74725-26-1; **13b**, 74725-27-2; **14a**, 74725-28-3; **14b**, 74725-29-4; **15a**, 65886-85-3; **15b**, 65886-87-5; **16**, 74725-30-7; **17**, 74725-31-8; **18a**, 61603-44-9; **18b**, 61603-45-0; **19**, 61603-52-9; **20**, 57867-57-9; **21**, 65886-86-4; **26**, 5296-51-5; **27**, 65886-89-7; **28a**, 74778-31-7; **28b**, 74725-32-9; **29a**, 57867-59-1; **29b**, 74725-33-0; **29c**, 65886-91-1; **29d**, 74725-34-1; **31a**, 74725-35-2; **31b**, 74725-36-3; **33**, 74725-37-4; **34**, 74725-38-5; **35a**, 74725-39-6; **35b**, 74725-40-9; **35c**, 74725-41-0; **36**, 74725-42-1; **37**, 74725-43-2; **38**, 33689-28-0; **39a**, 74725-44-3; **40**, 74725-45-4; **41**, 74725-46-5; **42**, 74725-47-6; **43**, 61603-46-1; **44**, 61603-47-2; **45**, 61603-48-3; **46a**, 61603-49-4; **46b**, 74725-48-7; **47a**, 74725-49-8; **47b**, 74725-50-1; **48a**, 74725-51-2; **48b**, 74725-52-3; **48c**, 74725-53-4; **49**, 61603-51-8; **50a**, 61603-50-7; **50b**, 885-90-5; **50c**, 613-12-7; **52**, 74725-54-5; **53**, 74725-55-6; **54**, 74725-56-7; **55**, 74725-57-8; **56**, 74725-58-9; sulfur dioxide, 7446-09-5; 4-phenyl-1,2,4-triazole-3,5-dione, 4233-33-4; dimethyl cyclobut-1-ene-1,2-dicarboxylate, 1128-10-5; benzenediazonium-2-carboxylate, 1608-42-0; 1,3-cyclohexadiene, 592-57-4; 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene, 40229-61-6; 7,8-dibromobicyclo[4.2.0]octa-2,4-diene, 27587-70-8; bicyclo[4.2.0]octa-2,4-diene, 3725-28-8; maleic anhydride, 108-31-6.

Electrolysis of Potassium Butyrate in Acetonitrile. A Deuterium NMR Study

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The anodic oxidation of 2,2-dideuteriobutyrate ion in acetonitrile gives rise to radical-derived and cation-derived C_3 products. By ^2H FT NMR spectroscopy, the radical-derived propane and propene are found to be formed without scrambling of the label. Similarly, the products derived from the intermediate isopropyl cation, i.e., the remainder of the propene and *N*-isopropylamides, bear deuterium only at the terminal C-1 and C-3 positions of the C_3 fragment. However, the 1:1:1 label distribution found in the *N*-*n*-propylamides and the formation of cyclopropane strongly suggest that ring closure of the *n*-propyl cation to rapidly scrambling protonated cyclopropane is an important reaction pathway. Atom scrambling at the level of protonated cyclopropane shows a large H/D isotope effect.

Introduction

The fundamental structures and interconversions of cationic C_3H_7 species have received much attention, both from experimental[1-3] and theoretical viewpoints.[4-6] There is general agreement that the *n*-propyl cation (**1**) is the highest metastable species on the ground-state energy

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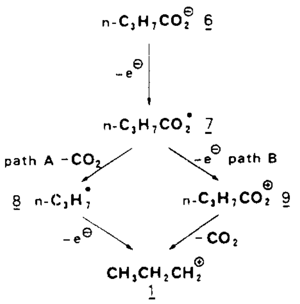
(1) (a) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969), and references cited therein; (b) C. C. Lee, *Prog. Phys. Org. Chem.*, **7**, 129 (1970); (c) J. L. Fry and G. J. Karabatsos in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1970, Chapter 14.

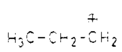
(2) (a) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972); (b) H. C. Brown, *Tetrahedron*, **32**, 179 (1976).

(3) (a) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973); (b) G. P. K. Smith, J. Weiner, M. Saunders, and R. J. Cross, *J. Am. Chem. Soc.*, **97**, 3593 (1975).

Scheme I



surface. More recent interest has focused on its ring closure to protonated cyclopropane (**2** or **3**) and its implication in dynamic atom scrambling of the isopropyl ion (**5**), the most stable member of the family of isomers.[3-5]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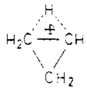
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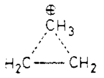
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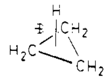
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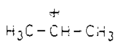
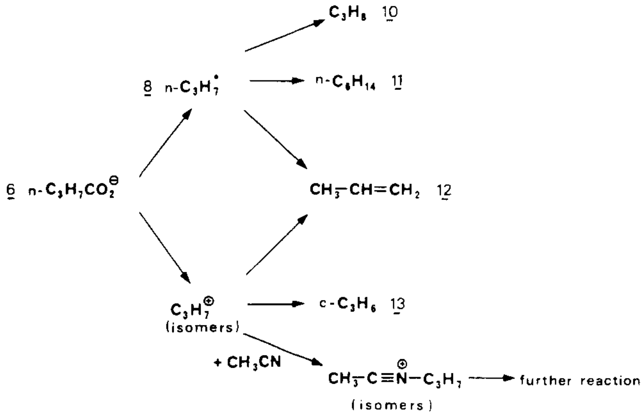

5

In a number of deaminations,[7] deoxidations,[8] and solvolysis reactions[9] of labeled *n*-propyl substrates, products have been obtained whose isotope distribution can only be interpreted by invoking formation of intermediate protonated cyclopropane. Further and convincing support for the implication of such a hypervalent intermediate comes from the direct protonation of cyclopropane itself.[10] Thus the existence of protonated cyclopropane is by now uncontested, and there are good indications that it is lower in heat of formation by some 8 kcal/mol than the open-chain primary ion **1** but thermodynamically less stable by another 8 kcal/mol than the isopropyl species **5**.[4-6,11] Nevertheless, the question of the precise nature of protonated cyclopropane remains a puzzle.[1] Whereas theoretical considerations[4-6] and the impressive amount of experimental work allow us to rule out the face-protonated cyclopropane (**4**), it is not possible to choose clearly between the edge-protonated species (**2**) and the corner-protonated one (**3**).

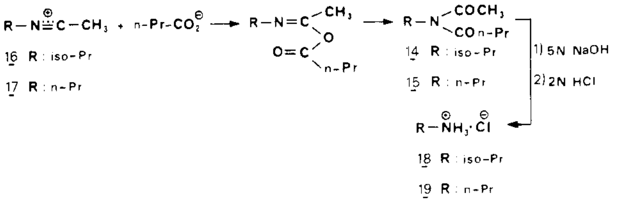
Ab initio calculations at the 6–31 G* level favor structure **3** over **2**,[4b] whilst CEPA-PNO[5] and the semiempirical MINDO/3 method[6b] assign a lower energy to the edge-protonated form **2**.

Two points have greatly complicated deamination[7] and solvolytic studies[9] in this field. Firstly, when starting from open-chain *n*-propyl substrates, the passage through free cations often only constitutes a minor process. Most of the *n*-propyl products result from direct S_N2-type reaction. Consequently, there is little observable isotope redistribution in *n*-propyl products. Secondly, stabilization of the cationic system by either solvation or pairing with the counterion can prolong lifetimes sufficiently to allow for the edge- or corner-protonated species to scramble their hydrogen atoms.[9c,12] Information about the intermediate, initially formed by ring closure of **1**, is thereby obscured.

Scheme II



Scheme III



In a recent paper[13] we have suggested that both of these drawbacks may possibly be reduced to a minimum when the primary carbocation is generated by the electrochemical route. In fact, it is now well-known that anodic oxidation of carboxylates such as **6** generates poorly solvated free carbocations at the electrode surface.[12] This may occur by either of the paths depicted in Scheme I.[14a,20]

Decarboxylation may follow immediately after the initial one-electron transfer to produce the *n*-propyl radical (**8**), which is then further oxidized (path A), or decarboxylation may take place after the second electron transfer via the acyloxonium ion (**9**; path B). Regardless of which pathway (A or B) is the correct one, there is clearly little chance for S_N2-type reactions to intervene. Moreover, sizeable amounts of cyclopropane are formed during the electrolysis of butyric acid.[13,15] This probably originates from deprotonation of either **2** or **3** and thus suggests that ring closure of **1** is important under these conditions.

In order to learn more about the nature and dynamics of the postulated $C_3H_7^+$ species, we have now carefully reexamined the electrooxidation of potassium butyrate and 2,2-dideuteriobutyrate in acetonitrile. Products, after isolation, were examined by NMR spectroscopy, including the direct observation of deuterium[16] in magnetic fields up to 9.39 T.

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[4] (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972); (b) P. C. Hariharan, L. Random, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 599 (1974); (c) H. Schwarz, W. Franke, J. Chandrasekhar, and P. v. R. Schleyer, *Tetrahedron*, **35**, 1969 (1979).

[5] H. Lischka and H. J. Köhler, *J. Am. Chem. Soc.*, **100**, 5297 (1978).

[6] (a) N. Bodor and M. J. S. Dewar, *J. Am. Chem. Soc.*, **93**, 6685 (1971); (b) P. K. Bischof and M. J. S. Dewar, *ibid.*, **97**, 2278 (1975).

[7] (a) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964); (b) C. C. Lee, J. E. Kruger, and E. W. C. Wong, *ibid.*, **87**, 3985 (1965); C. C. Lee and J. E. Kruger, *ibid.*, **87**, 3986 (1965); (c) G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *ibid.*, **92**, 606 (1970); (d) A. G. Meek, Z. Z. Martin, H. A. Nadworny, and M. S. Silver *J. Org. Chem.*, **41**, 323 (1976).

[8] P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959); **82**, 2971 (1960); **84**, 3962 (1962).

[9] (a) C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966); (b) C. C. Lee and W. K. Y. Chwang, *ibid.*, **48**, 1025 (1970); C. C. Lee and J. Law, *ibid.*, **49**, 2746 (1971); (c) C. C. Lee, A. J. Cessna, E. C. F. Ko, and S. Vassie, *J. Am. Chem. Soc.*, **95**, 5688 (1973).

[10] (a) R. L. Baird and A. A. Aboderin, *Tetrahedron Lett.*, 235 (1963); (b) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964); (c) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968); (d) N. D. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968).

[11] P. P. Dymerski, R. M. Prinstein, P. F. Bente III, and F. W. McLaffery, *J. Am. Chem. Soc.*, **98**, 6834 (1976).

[12] J. T. Keating and P. S. Skell, Vol. 2, "Carbonium Ions", Wiley, New York, 1970, (a) p 607; (b) pp 577, 678.

[13] E. Laurent and M. Thomalla, *Tetrahedron Lett.*, **1975**, 4411.

[14] J. H. P. Utley "Techniques of Electroorganic Synthesis", N. L. Weinberg, Ed., Wiley-Interscience, New York, 1974, Part I, (a) p 838; (b) p 828.

[15] W. J. Koehl, *J. Am. Chem. Soc.*, **86**, 4686 (1964).

[16] (a) P. Diehl in "Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Protons", T. Axenrod and G. A. Webb, Eds., Wiley, New York, 1974, Chapter 18, p 275; (b) H. H. Mantsch, H. Saitô, and I. C. P. Smith, *Prog. Nucl. Magn. Reson. Spectrosc.*, **11**, 211 (1977).

Table I. Yields and Relative Deuteration of Electrolysis Products of Butyrate Ion and 2,2-Dideuteriobutyrate Ion, Respectively, in Acetonitrile[a]

compd		% yield	relative ^2H distribution (percent) in the deuterated series for position: A	B	C	D
10	$H_3CCH_2CH_3$ A B A	15.0 ± 2	100	0		
11	$(H_3CCH_2CH_2\text{-})_2$ C B A	1.7 ± 0.5	100	0	0	
12	A H CH$_3$ D \ / C=C / \ B H H C	57.5 ± 5	33.8	34.8	0	31.4
13	CH$_2$ A / \ A H$_2$C—CH$_2$ A	6.6 ± 1	100			
14	A H$_3$C COCH$_3$ \ / CH—N / B \ A H$_3$C COCH$_2$CH$_2$CH$_3$	11.2 ± 0.3	100[b]	0		
15	COCH$_3$ / H$_3$CCH$_2$CH$_2$—N C B A \ COCH$_2$CH$_2$CH$_3$	3.0 ± 0.2	37.1[b]	30.4	32.5	
	acetamides + butyramides	<5.0 (total)				

[a] Total deuterium content of each molecule or group shown is normalized to 100%. [b] Determined after conversion into alkylammonium chlorides **18d** and **19d** (Scheme III).

As reported[13,17] several types of reaction are responsible for the products observed (Scheme II). Dimerization and hydrogen abstraction of the *n*-propyl radical (**8**) produce *n*-hexane (**11**) and propane (**10**). The propyl radical may also afford propene (**12**), owing to disproportionation.

Deprotonation of cationic C_3H_7 species is an additional source of propene (**12**) and, as stated above, accounts for the formation of cyclopropane (**13**). Finally, part of the cationic C_3H_7 species is intercepted by acetonitrile in a Ritter reaction[17,18] and appears bound to nitrogen in a variety of products in the condensed phase.

Results

The anodic oxidation of buffered potassium butyrate in acetonitrile containing 3% water produces at low current density the products listed in Table I. Besides the hydrocarbons (**10**–**13**) already mentioned, the two *N*-alkyl-*N*-acetylbutyramides **14** and **15** are of importance. They are formed by reaction of the corresponding nitrilium ions **16** and **17** with unconsumed butyrate in a Chapman-type reaction (Scheme III). Small amounts of secondary acetamides and butyramides are also formed but have not been analyzed further. They clearly result from hydrolysis of **14**, **15**, **16**, or **17** and therefore are not expected to provide additional information concerning the nature of the intercepted $C_3H_7^+$ species.

When potassium 2,2-dideuteriobutyrate (**6d**) was used as substrate in the electrolysis, the corresponding labeled products (**10d**–**15d**) were obtained. After separation of the gaseous fraction and careful purification of the mixture of the isomeric adducts **14d** and **15d**, the label distribution was determined from the proton noise-decoupled ^2H FT NMR spectra (Table I).

For illustration of this powerful analytical technique,[16] the spectra of the gaseous fraction (**10**, **12**, and **13**), condensed under pressure in CCl_4, are shown in Figure 1. The assignment of the ^2H resonances was made on the basis of the 1:1 relationship between the chemical shifts of ^1H and ^2H.

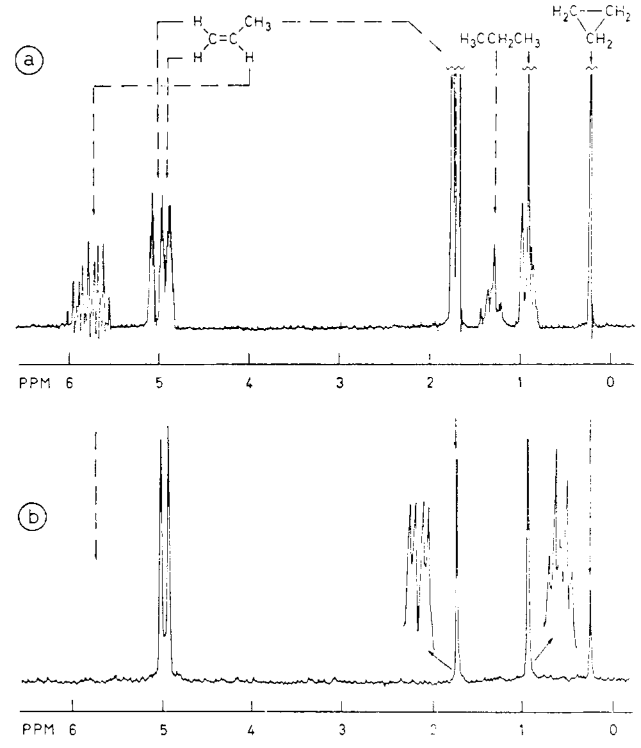

Figure 1. (a) ^1H NMR spectrum of the mixture of undeuterated **10**, **12**, and **13** in CCl_4 under pressure at 100 MHz. (b) Proton noise-decoupled ^2H FT NMR spectrum of the mixture of deuterated **10d**, **12d**, and **13d** in CCl_4 under pressure at 15.4 MHz. Inserts in b, proton-coupled 2 H resonances.

Propene (**12d**) is found to be labeled to the largest extent at the terminal olefinic positions but not at all at the central carbon atom. Propane (**10d**) turns out to be deuterated exclusively at C-1. Finally, cyclopropane (**13d**) appears with its single resonance at highest field. It is

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(17) J. M. Kornprobst, A. Laurent, and E. Laurent-Dieuzeide, *Bull. Soc. Chim. Fr.*, 3657 (1968); 1490 (1970).

(18) H. G. Thomas, *Angew. Chem., Int. Ed. Engl.*, 10, 557 (1971).

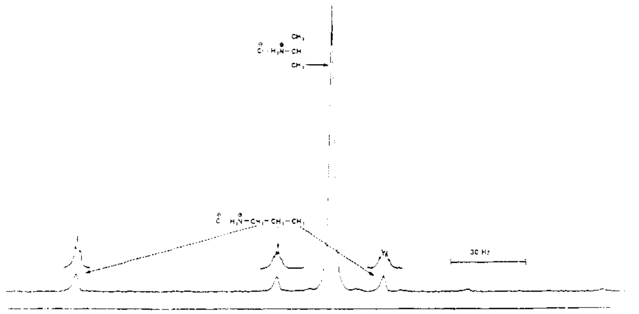


Figure 2. Proton noise-decoupled ^2H FT NMR spectrum of the mixture of alkylammonium chlorides **18d** and **19d** in water at 61.4 MHz. Inserts, fine structure of the proton-coupled ^2H resonances.

possible to obtain further information from the fine structure of the proton-coupled ^2H NMR spectra (inserts in Figure 1b). The ^2H signal of the methyl group of propene, for instance, appears as a doublet of doublets. Consequently, the position must be doubly deuterated. Similar information is somewhat more difficult to elicit for the other resonances, owing to the very small $^1H-^2H$ coupling constants and the more complex spin systems involved.

^2H FT NMR spectra have also been obtained for **14d** and **15d**. The butyryl grouping of these compounds comes directly from unelectrolyzed butyric acid (Scheme III) and therefore shows full labeling at the butyryl α carbon atom, thus masking somewhat the signals of interest.

As only the isopropyl and *n*-propyl groupings directly bound to nitrogen in **14d** and **15d**, respectively, are informative for our purpose, we have converted these isomers into the alkylammonium chlorides **18d** and **19d** and determined the label distribution at that level. An additional advantage of looking at the small ammonium ions **18d** and **19d** instead of the larger molecules **14d** and **15d** resides in the shorter reorientational correlation times of the former compounds and the resulting sharpness of the ^2H resonance lines[16] (Figure 2).

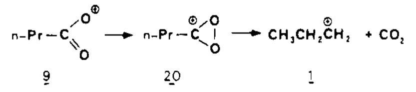
In the proton-coupled ^2H FT NMR spectrum of **19d** (inserts in Figure 2), the resonances at the three sites C-1, C-2, and C-3 show fine structures very close to a triplet, a sextet, and a doublet of triplets, respectively. This is what one would expect for geminally labeled isotopomers. Clearly, the deuterium atoms preferentially stay together throughout the process leading from 2,2-dideuteriobutyric acid to **19d**. (This point is confirmed by the ^{13}C NMR spectrum of **19d** recorded at 88 MHz on a CAMECA spectrometer.)

Interpretation and Discussion

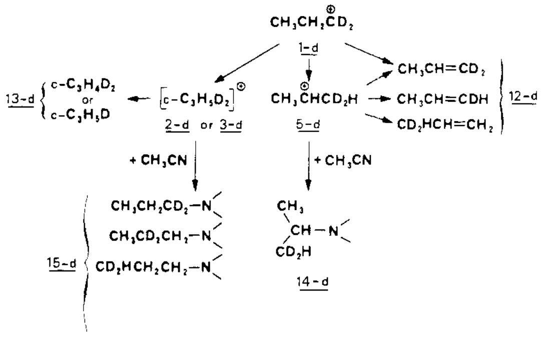
Radical Processes. Propane (**10d**) obtained from the electrolysis of 2,2-dideuteriobutyric acid is labeled exclusively at the terminal carbon atom. From the fine structure of the proton-coupled ^2H FT NMR spectrum (Figure 1b), we deduced that there must be two geminal deuterium atoms present. Therefore, propane results simply from the *n*-propyl radical, by hydrogen abstraction from the solvent, or by disproportionation.[14b,19] No label scrambling had occurred throughout the entire radical process. The intermediacy of the propyl radical is furthermore illustrated by the formation of small amounts of *n*-hexane (**11**).

Propene (**12**), however, has a multiple origin. For the radical disproportionation process mentioned above, we would expect **12d** to be labeled exclusively at the terminal olefinic positions. Experimentally, much label is also found in the methyl group of **12d** (Table I). Moreover, the amount of propene formed exceeds by far the yield of propane. This requires that the olefin has at least one other origin, which therefore should be ionic in nature.

Scheme IV



Scheme V



Origin of the Cationic C_3H_7 Species. It was pointed out in the introduction that two closely related anodic processes may lead to carbocations (Scheme I). Only oxidation of the propyl radical (**8**) or its precursor, the acyloxy radical (**7**), needs to be considered.[20] As label scrambling does not occur for either pathway prior to the moment when the *n*-propyl cation (**1**) is formed, the alternative mechanisms differ only in timing and no distinction can be made on the basis of the present product analysis alone. Nevertheless, we have a slight preference for path B (Scheme I), i.e., successive transfer of two electrons followed finally by decarboxylation. The reasons for this are as follows. The butyrate ion will, on electrostatic grounds, approach the anode surface with its carboxylic end ahead. If decarboxylation follows immediately after the first electron transfer, as would be required for path A, then time would be gained for desorption, thus preventing the second electron transfer to occur. More importantly, the propyl radical would be kept away from the anodic surface by the CO_2 fragment. In addition, alkyl radicals are known to have, at least in the gas phase, a fairly high ionization potential (>8 eV).[21] For path B, in contrast, the initial orientation of the butyryl anion at the electrode surface is the one required for the first and second electron transfer to occur in a fast consecutive manner. The final decarboxylation step (**9** → **1**) has recently been the subject of an ab initio MO study[22] and is believed to occur with high efficiency via the dioxiryl cation (**20**) (Scheme IV).

Ionic Processes. Let us now examine those compounds that result from deprotonation or trapping of the cationic C_3H_7 species. Clearly, there are two kinds of products present: first those that bear no deuterium labeling at the central carbon atom of the C_3 fragment, i.e., propene (**12d**) and the *N*-isopropyl derivative **14d**; secondly, those that show the label spread more or less between all sites, i.e., the *N*-*n*-propyl derivative **15d** and probably cyclopropane (**13d**). The occurrence of **14d** is a good indication of the

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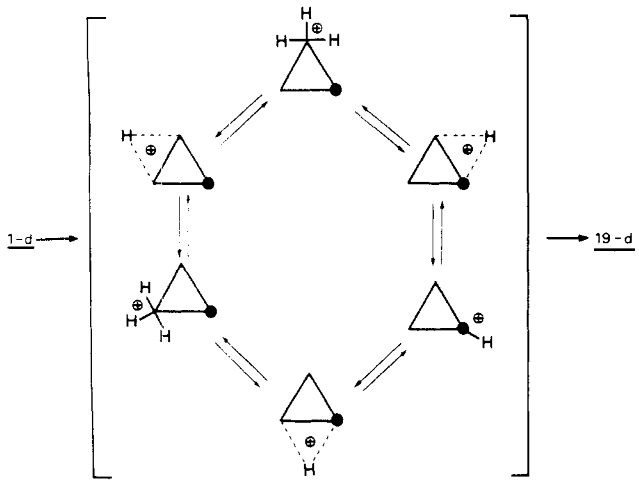
[19] L. Eberson in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, 1973, p 470.

[20] S. D. Ross, M. Finkelstein, and E. J. Rudd, "Anodic Oxidation", Academic Press, New York, 1975, p 156, and ref cited therein.

[21] P. Bischof, *J. Am. Chem. Soc.*, **98**, 6844 (1976).

[22] (a) W. F. Maier and M. T. Reetz, *J. Am. Chem. Soc.*, **97**, 3687 (1975); (b) L. Eberson and H. Schäfer, *Forschr. Chem. Forsch.*, **21**, 1 (1971).

Scheme VI



● : CD_2 (the slow deuterium migration is not shown)

intermediacy of an isopropyl cation. According to Scheme V, this simply results from 1,2 hydride shift of the very first *n*-propyl cation (**1d**) generated. The two geminal deuterium atoms stay together in **14d**.

Propene (**12d**), in addition to its radical origin mentioned above, will also be formed from the isopropyl cation (**5d**). It is this process that leads to geminal dideuteration of the methyl group of propene. In fact, deprotonation of independently generated secondary ions has been shown to be appreciable under electrolytic conditions.[23]

Quite different from the fairly transparent provenance of **12d** and **14d**, the *N*-*n*-propylamide (**15d**) cannot result directly from any of the classical ions **1d** or **5d**, and hence a third species, i.e., the protonated cyclopropane (**2d** or **3d**), must be invoked.

It was seen from the ^2H FT NMR spectrum of **19d** that the deuterium distribution in the *N*-*n*-propyl grouping is close to 1:1:1 with respect to the three carbon sites of the chain [$H_3C(3)$-$H_2C(2)$-$H_2C(1)$-N, found C-3 (32.5%), C-2 (30.4%), C-1 (37.1%)]. Note that this differs markedly from the 3:2:2 abundance of hydrogen in an *n*-propyl grouping.

In addition, the fine structure of the proton-coupled ^2H resonances of **19d** revealed that the two deuterium atoms have a strong tendency to remain geminal.

These findings allow for two conclusions. First, the hydrogen scrambling of protonated cyclopropane, generated by the electrochemical route, is too fast to permit distinction of whether the corner- or the edge-protonated species was formed first. That is to say, the experiment does not tell us where we entered and where we left the scrambling system depicted in Scheme VI. On the other hand, the scrambling shows a large isotope effect and is essentially concerning the hydrogen and not the deuterium atoms. Separation of the latter from geminal to vicinal sites apparently had not occurred to any major extent.

Conclusion

We may now summarize the events. Primary radical and ionic intermediates are generated from poorly or nonsolvated precursors at the anodic surface. They evolve further during the desorption from the electrode.

The primary cation **1** is clearly located in an energetically very high area of the $C_3H_7^+$ potential surface.[4-6] Its only option during desorption from the electrode is to undergo unimolecular decay. The latter is multiple in nature and thus suggests **1** to be a real intermediate.[3a] Proton extrusion possibly produces part of the propene. A competitive 1,2 hydride shift generates the most stable isomer of the $C_3H_7^+$ series, the isopropyl cation **5**. This in turn gives rise to the remainder of the propene and after reaction with solvent produces **14**. The third way in which the primary cation **1** can stabilize itself is ring closure to protonated cyclopropane.

Actually, the species involved in electrolysis seems to be close in its freeness to the unsolvated propyl cation obtained from the gas-phase radiolysis of butane.[24] The ring closure to protonated cyclopropane amounts, in this latter case, to 18–26% relative to the isopropyl cation formed. This percentage is markedly larger than that, for instance, in the case of the trifluoroacetolysis of propyl mercuric perchlorate[9c] but is comparable to the value found for the present electrolysis experiment (24–28%). This suggests that the energetics of the formation of intermediates are similar for radiolysis[24] and electrolysis.

Experimental Section

Spectroscopic and Spectrometric Methods. Infrared spectra were recorded on a Perkin-Elmer Model 337 instrument and are expressed in cm^{-1}. Correct molecular weights for all new compounds and labeled products were obtained by mass spectrometry performed on a Varian Mat CH5 instrument at 70 eV.

^1H NMR spectra were recorded in CCl_4 (unless otherwise stated) on a Varian Model T-60 or Varian Model XL-100 instrument at 60 MHz and 100 MHz, respectively. Chemical shifts are given in δ (parts per million) relative to internal Me_4Si.

Proton noise-decoupled ^{13}C FT NMR, spectra were recorded in $DCCl_3$ on a Varian Model XL-100 instrument at 25.2 MHz. Chemical shifts are expressed in δ (parts per million) relative to internal Me_4Si. Assignments are based on the off-resonance decoupling experiments.

^2H FT NMR spectra[16] were obtained at 15.4 MHz on a Varian Model XL-100 spectrometer or at 61.4 MHz on a Bruker WH-400 spectrometer by accumulation and Fourier transformation of 100 to 1000 free-induction decays. Sufficient deuterium relaxation was ensured by 16-s repetition intervals of the 90° pulses. ^1H decoupling was achieved by application of a weak noise-modulated RF field at the ^1H resonance (100 and 400 MHz, respectively). The ^{19}F resonance (94.1 MHz) of external hexafluorobenzene was used on the XL-100 spectrometer for field-frequency stabilization. ^2H FT NMR spectra at 61.4 MHz were obtained in an unlocked mode. ^2H chemical shifts are expressed in δ (parts per million) relative to perdeuterio Me_4Si, if not otherwise stated. In practice, internal $DCCl_3$ was used as reference.

Syntheses. 2,2-Dideuteriobutyric Acid. Benzyl propionate (75 mL, 0.48 mol) was added to a stirred suspension of 10 g (0.24 mol) of lithium aluminum deuteride (Fluka, 99% D) in 800 mL of dry ether. After reflux for 5 h, the mixture was hydrolyzed by successive addition of 10 mL of water, 10 mL of 15% NaOH solution, and again 30 mL of water.[25] From the dried ether layer 1,1-dideuteriopropanol (0.2 mol) was isolated by distillation. Reaction of this alcohol with a 3.3:1 mixture of 48% aqueous HBr solution and concentrated sulfuric acid produced the 1,1-dideuterio-*n*-propyl bromide.[26] This alkyl halide was transformed into its Grignard compound, which then was carboxylated by addition of dry ice. After acid hydrolysis and extraction, 9.3 g (0.10 mol) of 2,2-dideuteriobutyric acid was isolated by distillation. Further purification was achieved by GLC (20% FFAP on Chromosorb W, 35/60).

The ^1H NMR and mass spectra showed this product to be doubly deuterated in the α-C position to more than 98%. The

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(23) G. Bodennec, A. Laurent, *Bull. Soc. Chim. Fr.*, **1971**, 1691.

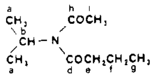
(24) S. G. Lias, R. E. Rebbert, and P. Auslos, *J. Am. Chem. Soc.*, **92**, 6430 (1970).

(25) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p 584.

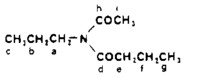
(26) A. I. Vogel, "Practical Organic Chemistry", Longmans, London, 1964, p 278.

IR spectrum (neat) showed characteristic absorptions at 3000 (OH), 1700 (C=O), and 2120 (C—D) cm^{-1}.

***N*-Isopropyl-*N*-acetylbutyramide (14).** Samples of 14 have been synthesized by an independent route as reported:[17] ^{1}H NMR (CCl_4) 0.94 (t, 7 Hz, H$_g$), 1.37 (d, 7 Hz, H$_a$), 1.63 (sextet, 6.5 Hz, H$_f$), 2.24 (s, H$_i$), 2.59 (t, 6.5 Hz, H$_e$), 4.21 (septet, 7 Hz, H$_b$); ^{13}C NMR ($DCCl_3$) 13.6 (C$_g$), 18.4 (C$_f$), 20.4 (C$_a$), 26.5 (C$_i$), 39.8 (C$_e$), 49.1 (C$_b$), 172.4 (C$_h$), 175.9 (C$_d$).



***N*-*n*-Propyl-N-acetylbutyramide (15).** Butyryl chloride (22 g, 0.2 mol) was added to 25 g (0.2 mol) of *N*-*n*-propylacetamide in the presence of 15.5 mL (0.2 mol) of anhydrous pyridine. After 5 h of reflux, the cold reaction mixture was treated with water and extracted with ether. After removal of the solvent from the dried organic layer, **15** was purified by column chromatography (silica gel, Merck 60, 0.063-0.2). The yield was 55 mmol (27%). The product gave correct elemental and mass spectral analyses. Futher characterization is based on its IR absorption (neat) at 1690 (C=O) and both ^{1}H NMR and ^{13}C NMR spectra: ^{1}H NMR (CCl_4) 0.9 and 0.92 (t, 6.5 Hz, H$_c$ and H$_g$), 1.2–2.0 (m, H$_b$ and H$_f$), 2.3 (s, H$_i$), 2.63 (t, 7 Hz, H$_e$), 3.61 (t, 7.5 Hz, H$_a$); ^{13}C NMR ($DCCl_3$) 11.3 (C$_c$), 13.7 (C$_g$), 18.3 (C$_f$), 22.6 (C$_b$), 26.4 (C$_i$), 39.5 (C$_e$), 46.0 (C$_a$), 172.4 (C$_h$), 175.9 (C$_d$).



Electrolysis. General. The electrolyses were performed in a closed 300-mL Tacussel reactor system equipped with a thermostated (25 °C) double-wall water jacket and a magnetic stirrer. The chamber of the Pt anode was separated from the cathode by an alumina crucible and equipped with a gas carrier system. The anodic potential was kept constant at 2 V relative to the calomel electrode (potentiostat, Tacussel Model PRT 40-1X). The current used in the electrolysis was determined by means of an in-line integrator placed in the cathodic circuit.

Electrolyses were performed on 300-L solutions of 30–50 mmol of butyric acid in the presence of 30 mol% potassium hydroxide in wet acetonitrile (3% (v/v) water). Gaseous products were swept from the anode chamber by a weak current of nitrogen. After passage through a $CaCl_2$/Ascarit tower, they were collected in a trap system cooled with liquid air. Redistilled samples were used for mass spectrometry and NMR analysis, the latter being condensed into CCl_4 and then sealed. The relative composition of the gaseous mixture was determined by ^{1}H NMR integration. Absolute yields are based on the material balance.

Acetonitrile was removed from the liquid phase of the reaction mixture by vacuum distillation. The products were then dissolved in methylene chloride and treated with 5% aqueous sodium bicarbonate solution to eliminate any remaining butyric acid. After the organic layer was dried over $MgSO_4$ and the solvent was removed, the products were purified by chromatography. Either column chroamtography on silica gel (Merck 60, 0.063-0.2) or preparative TLC on silica gel (Merck 60) was used. Unelectrolyzed butyric acid was recovered from the aqueous phase by acidification and exhaustive extraction with CH_2Cl_2.

The identification of all products is based on comparison of their chromatographic, mass spectrometric, and NMR spectroscopic features with authentic samples.

Electrolysis of Butyric Acid. Butyric acid (4.4 g, 50 mmol) was electrolyzed according to the general procedure given above. Starting material (25%) was recovered unchanged. The current used integrated to 8900 C; i.e., 2.5 electrons per molecule were consumed. The products and their yields after purification are compiled in Table I. In addition, a small quantity of *n*-propyl butyrate (<2%) was isolated from this run.

The ^{1}H NMR spectrum of the gaseous products is shown in Figure 1a. The ^{1}H NMR, ^{13}C NMR, and mass spectra of **14** and **15** (not separated from each other) are in full agreement with those of the authentic samples.

Electrolysis of 2,2-Dideuteriobutyric Acid. The labeled acid (2.9 g, 32 mmol) was electrolyzed as indicated in the general procedure above. Starting material (12%) was recovered when 4750 C had passed through the cell. This amounts to a pickup of 1.82 electrons per molecule.

The relative deuterium distribution in the products was determined from the computer-integrated ^{2}H-(^{1}H) FT NMR spectra and is compiled in Table I (see also Figure 1b and 2). The line intensities, isotope shift effects, and off-resonance multiplicities in the ^{13}C NMR spectra of **14d** and **15d** are in agreement with the deuterium distribution shown in Table I. However, quantitative information based on the ^{13}C NMR spectra, as reported in a preliminary note, is clearly less reliable than the direct ^{2}H NMR spectroscopic analysis presented here.

Registry No. 6, 461-55-2; **10**, 74-98-6; **11**, 110-54-3; **12**, 115-07-1; **13**, 75-19-4; **14**, 21855-95-8; **15**, 74432-12-5; 2,2-dideuteriobutyric acid, 19136-92-6; benzyl propionate, 122-63-4; 1,1-dideuteriopropanol, 40422-04-6; 1,1-dideuterio-*n*-propyl bromide, 40422-05-7; butyryl chloride, 141-75-3; *N*-*n*-propylacetamide, 5331-48-6; 2,2-dideuteriobutyrate ion, 58978-98-6.

Syntheses and Stereochemistry of Amidoximes

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The configuration and tautomeric structure of a variety of amidoximes have been examined. The compounds studied were simple acyclic amidoximes possessing alkyl substituents and cyclic amidoximes including thiomorpholines, piperazines, imidazolidines, and 2-iminothiazolidines. The syntheses of these novel amidoximes are described along with NMR determinations of the stereochemistry of the oxime moiety. Factors determining the configuration and tautomeric structure of amidoximes are also discussed.

Configuration (*E* vs. *Z* isomers), conformation, and tautomerism are important characteristics associated with amidoximes. Although amidoximes have been known since the late 1800's, a review by Eloy and Lenaers[1] in 1962 only briefly mentioned the tautomeric question and did not address the configuration and/or conformation problems. Considerable work has been done since 1960 in determining these properties for simple amidoximes such as benzamidoximes,[2-7] formamidoxime,[2-8] and *N*,*N*-di-

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(1) F. Eloy and R. Lenaers, *Chem. Rev.*, **62**, 155 (1962).

(2) O. Exner and N. Motekov, *Collect. Czech. Chem. Commun.*, **43**, 2740 (1978).

(3) O. Exner, *Collect. Czech. Chem. Commun.*, **30**, 652 (1965).

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