Organic and Biological Chemistry

The 3,3-Dimethyl-1-butyl Cation

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Abstract: The 3,3-dimethyl-1-butyl cations generated by anodic oxidation of the radical and by deoxideation show similar patterns of trapping, β cleavage, and double 1,2 rearangements over a wide range of solvent basicities; no 1,3-rearrangement product was detected (<0.01%). Product formation occurs from the cations: 3,3-dimethyl-1-butyl, 3,3-dimethyl-2-butyl (pinacolyl), 2,3-dimethyl-2-butyl, and *t*-butyl (from β cleavage). Both cation-generating procedures show characteristic alterations of product with changing solvent basicity with a sharp discontinuity at pH 14. It is postulated that the products are formed from free cation intermediates trapped by water below pH 14, by hydroxide ion above pH 14, hydroxide trapping showing a greater preference for deprotonation to produce mainly olefins. It is hypothesized that superimposed on this effect, by the steepening of the potential gradient at the anode with increasing pH, is an effect which alters the rates of the rearrangement and the β-cleavage processes. The free 4,4-dimethyl-2-pentyl cation shows similar behavior. The products from acetolysis and formolysis of 3,3-dimethyl-1-butyl tosylate are the unrearranged esters.

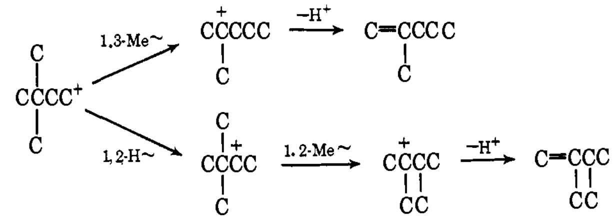
Studies of free carbonium ions under conditions that permit rapid trapping and no possibility for return of the products to carbonium ions are revealing the early behavior of these reaction intermediates. These intermediates are best studied in the presence of hydroxide ions, the products of the reaction $R^+ + OH^-$ being olefins and alcohols. Earlier it was reported that deoxideation by CX_2 was a useful method for making R^+ from ROH in basic media.[2,3] Anodic oxidation on a platinum surface also can be used to generate R^+ from RCO_2^- in basic media. The formation of carbonium ions in the abnormal Kolbe electrolysis has been recognized in a number of laboratories[4-10] and has been called the Hofer-Moest reaction.[11]

$$RCO_2^- \longrightarrow R\cdot + CO_2 + e^- \quad \text{(Kolbe)}$$

$$RCO_2^- \longrightarrow R^+ + CO_2 + 2e^- \quad \text{(abnormal Kolbe)}$$

Deoxideation of 2-methyl-1-butanol to 2-methyl-1-butyl cation in aqueous hydroxide solution demonstrated that 1,2-hydrogen, 1,2-methyl, 1,2-ethyl, and 1,3-hydrogen rearrangements occur in competition with trapping by hydroxide ion,[3,12] indicating the half-lives for the unimolecular rearrangements are less than 10^{-10} sec.[3,12] Anodic oxidation of potassium 3-methylpentanoate in alkaline solution results in formation of the same product mixture as obtained from deoxideation,[13] indicating a similar precursor. Another example, rich in the detail it provides for carbonium ion processes, is the anodic oxidation of potassium 4,4-dimethylpentanoate to the 3,3-dimethyl-1-butyl cation, an experiment originally designed to examine the importance of 1,3-methyl migrations. The 3,3-dimethyl-1-butyl cation also was generated by deoxideation.

1,3-Methyl Rearrangements. Because of the ambiguity of many 1,3-methyl rearrangements in carbonium ions,[14-19] the 3,3-dimethyl-1-butyl cation system[20] was chosen as an unambiguous system where different carbon skeletons would be obtained if 1,3 and/or successive 1,2 shifts were operative. A 1,3-methyl shift gives the 2-methyl-2-pentyl cation while successive 1,2 shifts lead to the 2,3-dimethyl-2-butyl cation.



Products other than those shown can be envisaged, but

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[1] From the Ph.D. Thesis of P. H. R., The Pennsylvania State University, 1967.

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[15] N. L. Drake, G. M. Kline, and W. C. Rose, *ibid.*, **56**, 2076 (1934).

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Table I. Carbonium Ion Products from Anodic Oxidation of Potassium 4,4-Dimethylpentanoate[a]

Products	Mole %[b]	Products	Mole %[b]
3,3-Dimethyl-1-butene	4.3	3,3-Dimethyl-2-butanol	1.0
3,3-Dimethyl-1-butanol	20.6	3,3-Dimethyl-2-butyl ester[c]	0.2
3,3-Dimethyl-1-butyl ester[c]	1.2	2,3-Dimethyl-1-butene	18.3
Ethene	26.0	2,3-Dimethyl-2-butene	0.1
2-Methylpropene	21.0	2,3-Dimethyl-2-butanol	3.5
2-Methyl-2-propanol	0.6	2,3-Dimethyl-2-butyl ester[c]	1.4
2-Methyl-2-propyl ester[c]	1.6		
			99.8

[a] pH 10, determined by narrow range pH papers; the pH did not change from beginning to end of electrolysis. [b] Percentages obtained from the experimental data (Table VIII) by subtracting the amounts of free-radical products (2,2,7,7-tetramethyloctane, 2,2-dimethylbutane, and a quantity of 3,3-dimethyl-1-butene equal to the amount of 2,2-dimethylbutane) and then adjusting the remainders to total 100%. [c] 4,4-Dimethylpentanoates.

the telltale carbon skeletons (2-methylpentyl or 2,3-dimethylbutyl) would be the bones of these, too.

Table I lists the carbonium ion derived products from anodic oxidation at a platinum electrode of potassium 4,4-dimethylpentanoate; product variation as a function of pH will be discussed separately.

Rearrangement of 3,3-dimethyl-1-butyl cation (primary) to 2-methyl-2-pentyl cation (tertiary) did not occur; products from the latter cation could not have accounted for more than 0.01% of the total.

Deoxideation[21] of 3,3-dimethyl-1-butanol (Table II), also producing the 3,3-dimethyl-1-butyl cation, failed to exhibit 1,3-methyl rearrangement; 2-methyl-1-pentene and 2-methyl-2-pentene were not products of the reaction. Likewise, deamination of 3,3-dimethyl-1-butylamine yielded no 2-methyl-2-pentanol;[20] Saunders[20] reported 3,3-dimethyl-1-butanol (56%) and 2,3-dimethyl-2-butanol (44%) (olefins were not mentioned). Solvolyses of 3,3-dimethyl-1-butyl tosylate gave no indications of a 1,3-methyl migration.

Table II. Deoxideation of 3,3-Dimethyl-1-butanol[a]

Olefins	Mole %
3,3-Dimethyl-1-butene	72.9
Ethene	3.1
2-Methylpropene	3.2
2,3-Dimethyl-1-butene	18.7
2,3-Dimethyl-2-butene	2.1
	100.0

[a] [KOH] = 19 *M*.

Although 1,3-hydrogen shifts are recognized as valid carbonium ion processes,[22] some proceeding through the intervention of protonated cyclopropanes,[23] 1,3-methyl shift has not been recognized in the 3,3-dimethyl-1-butyl and 4,4-dimethyl-2-pentyl (*vide infra*) cation systems.

The 3,3-Dimethyl-1-butyl Cation. While the 3,3-dimethyl-1-butyl cation does not show 1,3-methyl rearrangement, it does undergo two 1,2 shifts yielding 2,3-dimethyl-2-butyl cation; at pH 10, 31% of the 3,3-dimethyl-1-butyl cation produced by anodic oxidation underwent these rearrangements (Figure 1). The same double 1,2 shifts are observed in deoxideation and deamination[20] but insignificantly in acetolysis or formolysis of the corresponding tosylate (Table III).

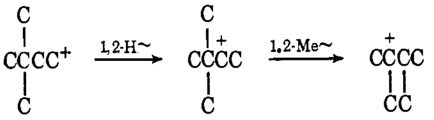
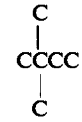
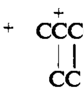


Table III. Relative Amounts of Successive 1,2 Shifts in 3,3-Dimethyl-1-butyl Cations

Method	Trapping agent	 Products	 Products
Anodic oxidation[a]	H_2O	1.0	0.98
Deamination[b]	H_2O	1.0	0.79
Deoxideation[c]	OH^-	1.0	0.27
Solvolysis[d]	RCO_2H	1.0	<0.02

[a] From Table I; both elimination (olefins) and substitution (alcohols and esters) products considered. [b] Only substitution products (alcohols) considered.[20] [c] From Table II; only elimination products (olefins) considered.[21] [d] Acetolysis or formolysis of tosylate: 1.9% yield of rearranged olefins may be products from pinacolyl tosylate contaminant; no rearranged esters found.

The presence of unrearranged products 3,3-dimethyl-1-butene, 3,3-dimethyl-1-butanol, and 3,3-dimethyl-1-butyl 4,4-dimethylpentanoate from the anodic oxida-

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(21) Deoxideation systems do not reflect the total product composition because only olefins are examined. Since high Br^- concentrations are developed during the reaction, the coupling, $R^+ + Br^-$, followed by dehydrobromination may make a contribution to the olefins; however under strongly basic conditions olefin formation from $R^+ + OH^-$ dominates.

(22) (a) For 1,3 shifts and cyclopropane formation see ref 2, 3, 9, 10, 12, and 13; O. A. Reutov and T. N. Shatkina, *Tetrahedron*, 18, 237 (1962); O. A. Reutov, "Congress Lectures, XIXth International Congress of Pure and Applied Chemistry," Butterworth and Co. (Publishers) Ltd., London, 1963, p 203; J. H. Bayless, F. D. Mendicino, and L. Friedman, *J. Am. Chem. Soc.*, 87, 5790 (1965); 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); M. Silver, *ibid.*, 83, 3487 (1961); G. J. Karabatsos, R. A. Mount, D. O. Richter, and S. Meyerson, *ibid.*, 88, 5651 (1966); G. J. Karabatsos, N. Hsi, and S. Meyerson, *ibid.*, 88, 5649 (1966); A. A. Aboderin and R. L. Baird, *ibid.*, 86, 2300 (1964). (b) J. T. Keating and P. S. Skell in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y., in press. (c) J. T. Keating, Ph.D. Thesis, The Pennsylvania State University, 1968.

(23) Protonated cyclopropanes: R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, 86, 252 (1964); A. A. Aboderin and R. L. Baird, *ibid.*, 86, 2300 (1964); R. L. Baird, *Tetrahedron Letters*, 235 (1963); C. C. Lee and J. E. Kruger, *Can. J. Chem.*, 44, 2343 (1966); *J. Am. Chem. Soc.*, 87, 3986 (1965); C. C. Lee, J. E. Kruger, and E. W. C. Wong, *ibid.*, 87, 3985 (1965); N. C. Deno and D. N. Lincoln, *ibid.*, 88, 5357 (1966); H. Hart and R. H. Schlosberg, *ibid.*, 88, 5030 (1966); P. S. Skell, I. Starer, and A. P. Krapcho, *ibid.*, 82, 5257 (1960); G. J. Karabatsos, R. A. Mount, D. O. Richter, and S. Meyerson, *ibid.*, 88, 5651 (1966); G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, 82, 1944 (1964); G. J. Karabatsos, N. Hsi, and S. Meyerson, *ibid.*, 88, 5649 (1966); S. Meyerson and H. Hart, *ibid.*, 85, 2358 (1963).

tion of 4,4-dimethylpentanoate (Table I) provides evidence that the free primary cation was trapped. The immediate precursor of the cation is the free radical. The vertical transition from radical to cation occurs over an interval of ~10^{-15} sec,[24,25] producing a carbonium ion subject only to the nominal encumbrance of the free radical. The amount of this primary cation trapped before rearrangement varied with pH between the limits of 19 and 40%. The earlier observation[20] that unrearranged alcohol is formed in the analogous deamination was not carried to an unambiguous conclusion regarding the intermediacy of a primary cation because the possibility of an SN2 displacement of N_2 from primary RN_2^+ could not be eliminated.[26] Because of the similarity of products from the three exothermic[27] cation-generating processes it is reasonable to discard the displacement possibility for deamination and deoxideation and to ascribe to each of these reactions a free primary cation intermediate. The failure to observe rearrangement in the solvolyses of 3,3-dimethyl-1-butyl tosylate is a basis for eliminating a free cation intermediate.

From the work in other primary tosylate systems it is apparent that solvolytic displacements occur without significant rearrangement.[26,28,29] This is understandable, since the cation is encumbered at birth and all subsequent stages of its existence.[27] The three other reactions produce poorly solvated (less encumbered or free[30]) 3,3-dimethyl-1-butyl cations, and the amount of rearrangement in these carbonium ions is inversely a measure of (1) the efficiency of the trapping agents in the environs of the cation and (2) the amount of encumbrance on the cation at birth. The relation of exothermicity of the cation-generating reaction to encumbrance at birth is treated elsewhere.[12] From energetics alone deamination gives a less encumbered carbonium ion than deoxideation. Encumbrance for anodic oxidation is variable with potential; this method can produce the least encumbered carbonium ion. However, the trend shown in Table III cannot be interpreted simply, because there are large differences in temperature and the efficiency of the trapping agents differ, deoxideations occurring in strong base, deaminations in weakly acidic media. The thesis is developed in detail elsewhere[12] that free cations in water-like systems become encumbered by neighbor nucleophiles in ~10^{-10} sec and these encumbered cations rapidly collapse to products (olefins, alcohols, esters, etc.). The encumbered cations are very similar to the intermediates in the endothermic cation-generating reactions as, for example, solvolyses. Encumbered cations lacking β branching collapse to products without significant amounts of rearrangement.[26,28,29] The distinctive reactions of free cations take place in the 10^{-10}-sec interval prior to the development of encumbrance.

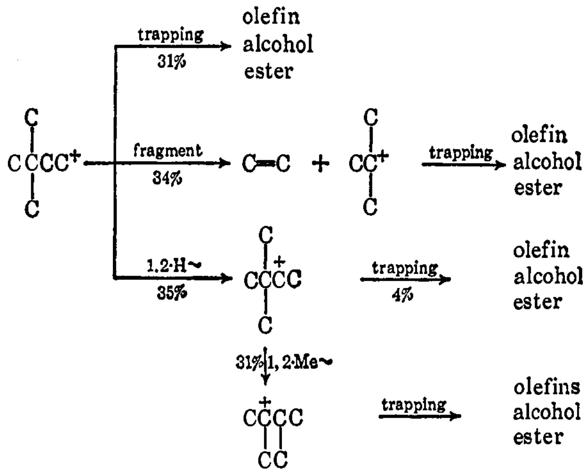

Figure 1. The 3,3-dimethyl-1-butyl cation generated by anodic oxidation, pH 10; data from Table I.

Pinacolyl Cation. Solvolyses of 3,3-dimethyl-2-butyl halides[31-33] or tosylate[32] produce only 2,3-dimethyl-2-butyl compounds, the rearrangement of pinacolyl cation being almost as facile as neopentyl cation rearrangement. These rearrangements to tertiary cations are sufficiently fast to compete with trapping of the original encumbered cations by nucleophiles. In anodic oxidations of potassium 4,4-dimethylpentanoate 13% of the 3,3-dimethyl-2-butyl (pinacolyl) cation is trapped: 3% alcohol, 1% ester, and 9% 3,3-dimethyl-1-butene (estimated by assuming the same ratio of alcohol to olefin as found in the direct generation of pinacolyl cation by anodic oxidation of 2,3,3-trimethylbutanoate).[34] Saunders had suggested a concerted rearrangement of 3,3-dimethyl-1-butyl cation (from deamination) to 2,3-dimethyl-2-butyl cation because he had failed to obtain any 3,3-dimethyl-2-butanol.[20]

Water and Hydroxide Ion Trapping. Electrolyses of potassium 4,4-dimethylpentanoate were conducted at various base strengths (pH 6.6–14.5; see Table IV);

Table IV. Electrolytically Generated 3,3-Dimethyl-1-butyl Cation

	% at pH						
Process	6.6	8.2	9.4	10.0	13.6	14.0	14.5
$3,3\text{-}Me_2\text{-}1\text{-}Bu^+$ trapping	39.9	35.2	30.2	31.5	19.0	37.8	39.7
Fragmentation	21.6	30.6	32.1	34.1	46.1	44.4	56.3
$3,3\text{-}Me_2\text{-}2\text{-}Bu^+$ trapping[a]	2.5	1.0	2.9	3.7	2.9	1.3	1.8
$2,3\text{-}Me_2\text{-}2\text{-}Bu^+$ trapping	35.9	35.2	34.8	30.7	32.0	16.5	2.3
Total	99.9	100.0	100.0	100.0	100.0	100.0	100.1

[a] The amount of 3,3-dimethyl-1-butene from 3,3-dimethyl-2-butyl cation was calculated by assuming that 3,3-dimethyl-2-butyl cation partitions itself between alcohol and olefin in the same ratio as found in the electrolysis of potassium 2,3,3-trimethylbutanoate.[34]

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(24) E. Sacher and K. J. Laidler in "Modern Aspects of Electrochemistry," No. 3, J. O'M. Bockris and B. E. Conway, Ed., Butterworth and Co. Publishers, Inc., Washington, D. C., 1964, p 8.

(25) R. A. Marcus in "Transactions of the Symposium on Electrode Processes," E. Yeager, Ed., John Wiley and Sons, Inc., New York, N. Y. 1961, p 239.

(26) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

(27) See ref 22b.

(28) C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966).

(29) R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

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(31) E. Linnemann, *Ann.*, **162**, 12 (1872).

(32) G. M. Calhoun and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **77**, 6441 (1955).

(33) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951).

(34) P. S. Skell and P. H. Reichenbacher, *J. Am. Chem. Soc.*, in press.

Table V. 3,3-Dimethyl-1-butyl Cation Generated by Deoxideation (Only Olefins)

Process	% at pH[a] 13.3	13.5	13.9	14.3	14.5	14.7	14.8	14.9	15.3
3,3-Me_2-1-Bu^+ trapping	30.9	31.5	31.5	30.8	32.2	53.5	62.5	67.7	75.2
Fragmentation	56.0	47.9	52.2	54.4	42.8	12.7	5.8	5.6	3.3
2,3-Me_2-2-Bu^+ trapping	13.0	20.6	16.3	14.8	25.0	33.8	31.7	26.6	21.5
Total	99.9	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0

[a] Calculated from the initial molarity of KOH; see Table X.

these changes influenced the relative amounts of products, both carbonium ion derived (Figure 2) and free radical derived (discussed later). Product variations as a function of hydroxide concentration in the deoxideations of 3,3-dimethyl-1-butanol were studied also; see Table V and Figure 2.

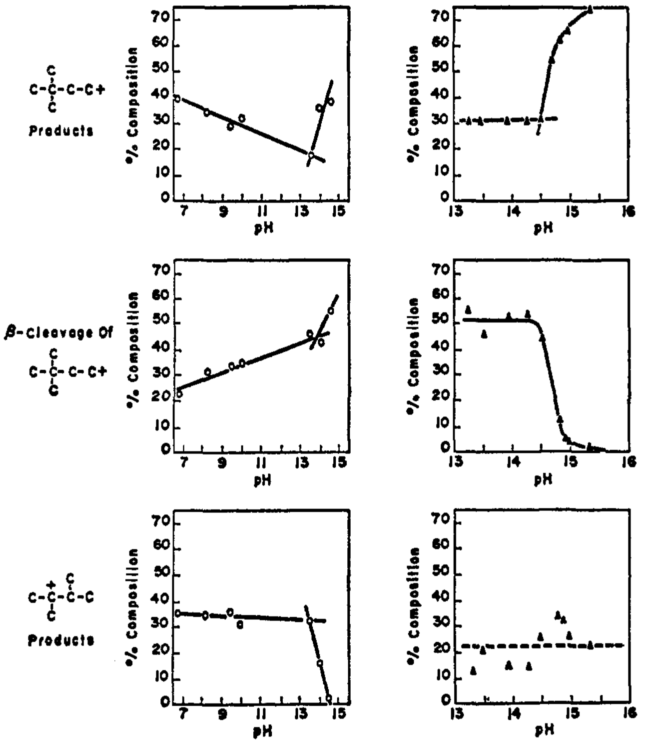


Figure 2. Variations of product ratios *vs.* pH: O, anodic oxidations of potassium 4,4-dimethylpentanoate (olefins, alcohols, esters); Δ, deoxideations of 3,3-dimethyl-1-butanol (olefins only).

The sharp discontinuity in these profiles which appears at pH 13.5–14.5 suggests two kinds of trapping. Although the break comes at different pH values for the two types of reactions, the difference probably appears greater than it really is since knowledge of OH^- concentrations is poor in these concentrated solutions which consume base during the reaction. The insensitivity of product composition to basicity below this pH leads to the postulate that water is the major trapping agent; above this pH, hydroxide ion trapping dominates. Above pH 13.5–14.5 the ratio of rearranged to unrearranged products decreases dramatically, indicating the greater effectiveness of hydroxide ion as a trapping agent. Rearrangement is a unimolecular process which competes favorably with the trapping of the initial cation by water and less favorably when hydroxide ion is the trapping agent. Accompanying this change of trapping agent is a change in selectivity, hydroxide ion showing a larger ratio of olefin to alcohol formation than is found for trapping by water (*vide infra*).

It may seem trivial to emphasize the greater reactivity of hydroxide ion, but as E_{act} diminishes, a leveling effect operates, and eventually rates become diffusion controlled. The reactions of alkyl cations with water and hydroxide undoubtedly fall in this latter category. Unfortunately there are few pertinent analogies. The reaction of H^+ with OH^- is perhaps the fastest chemical reaction,[35] but its great velocity is attributable to the Grotius transfer of H^+ through the medium. A rate

$$H^+ + OH^- \longrightarrow H_2O \qquad k = 1.4 \times 10^{11}\ M^{-1}\,\text{sec}^{-1}$$

factor of 10^6 separates the reactions of OH^- and H_2O with CO_2.[35] Perhaps more relevant is the 10^4 separa-

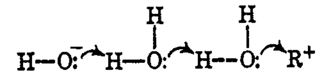
$$CO_2 + OH^- \longrightarrow HCO_3^- \qquad k = 1.4 \times 10^4\ M^{-1}\,\text{sec}^{-1}$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad k = 4.3 \times 10^{-2}\ \text{sec}^{-1}$$

$$(R^+) + OH^- \longrightarrow ROH \qquad k = 2.2\ M^{-1}\,\text{sec}^{-1}$$

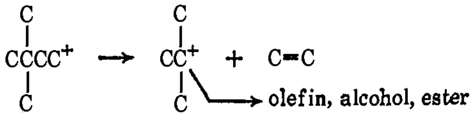
$$(R^+) + H_2O \longrightarrow ROH_2^+ \qquad k = 2.1 \times 10^{-4}\ \text{sec}^{-1}$$

tion of rates of trapping of triarylcarbonium ions by these bases.[36] In the present work it is clear that OH^- and H_2O trapping differ in both rate and selectivity. A Grotius-type transfer of OH^- may be operative at high hydroxide ion concentrations. On the other hand,



the rate of trapping by water is limited by the rate of molecular tumbling of water molecules in the highly hydrogen-bonded environment of aqueous systems.

β Cleavage. An important reaction of 3,3-dimethyl-1-butyl cation is fragmentation to ethene and 2-methyl-2-propyl cation, 20–55% of the cation processes in anodic oxidations and 3–50% in deoxideations. The reaction was not recognized in deamination[20] (probably not sought) and does not occur in solvolyses. In



deoxideations and below pH 13 anodic oxidations, the ratio of 2-methyl-2-propyl products to ethene is unity.

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(35) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, 3, 1 (1964); M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Progr. Reaction Kinetics*, 2, 287 (1964).

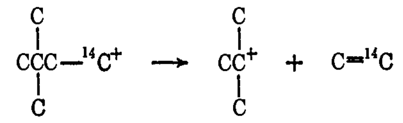
(36) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Am. Chem. Soc.*, 89, 2063 (1967).

Table VI. Elimination and Substitution Reactions of Carbonium Ions from Electrolyses of Potassium 4,4-Dimethylpentanoate

Cation	Elimination/substitution[a] at pH						
	6.6	8.2	9.4	10.0	13.6	14.0	14.5
3,3-Me_2-1-butyl (primary)	0.08	0.15	0.12	0.12	0.15	2.6	2.6
3,3-Me_2-2-butyl (secondary)	1.2	0.5	1.3	1.3	1.6	7.3	7.3
2-Me-2-propyl (tertiary)	1.9	3.0	6.0	9.0	6.7	19	99
2,3-Me_2-2-butyl (tertiary)	4.3	3.8	4.5	3.8	1.7	4.5	>100

[a] Substitution products are alcohol and ester.

Anodic oxidations above pH 13 give much higher ratios (up to 7:1). With ^{14}C labeling it was shown that, in those circumstances where the ratio is greater than unity,



$$(CH_3)_3C-{}^{14}CH_2^{+} \longrightarrow (CH_3)_3C^{+} + CH_2={}^{14}CH_2$$

$$C={}^{14}C \longrightarrow CO_2 + {}^{14}CO_2 + H_2O$$

ethene is very efficiently oxidized to CO_2 and H_2O, and thus the 2-methyl-2-propyl products are the best measure of extent of fragmentation. In fuel cell operation it is established that ethene is more readily oxidized than longer and branched-chain hydrocarbons.[37-39]

Quite striking is the difference in pH profile (Figure 2) of fragmentation for deoxideations and anodic oxidations, the former behaving normally in decreasing with increasing hydroxide ion concentration because of more effective trapping of the 3,3-dimethyl-1-butyl cation. The reverse is true for anodic oxidations carried out at high hydroxide ion concentrations. This observation leads to an intriguing possibility.

Fragmentation for gas-phase free 3,3-dimethyl-1-butyl cation is nearly thermoneutral;[12] this is a reasonable model for the free cation fragmentation in the condensed phase.[40] However, in anodic oxidations the cation is generated at the anode surface in a steep potential field. Fragmentation moves the charge away from the anode and thus the reaction becomes more exothermic than in the absence of the field. The potential gradient increases with increasing hydroxide ion concentration.[41,42]

The gradually increasing dominance of fragmentation in anodic oxidations over the range pH 6–13 (field gradient effect) forces a complementary decrease in the amount of 3,3-dimethyl-1-butyl cation which is trapped. The decrease is not as large in the rearranged products over this pH range because these too would be more exothermic in the steepened potential gradient.

The differences between the pH profiles for anodic oxidation and deoxideation can be explained by considering for the latter the change in trapping efficiency only; for the former there is superimposed on this effect a change of rearrangement and cleavage energetics and rates with field gradient changes at the electrode surface. This field effect is being examined further.

The cleavage of 4,4-dimethyl-2-pentyl cation (*vide infra*) to propylene and *t*-butyl cation is approximately 16 kcal/mole endothermic from the ethylene cleavage;[12] nonetheless, this anodically generated secondary cation does cleave, albeit approximately one-half as readily as the primary cation. The cleavage of the secondary cation could not be fast enough to occur under these trapping conditions (pH 14) were it not for the potentiating effect of the field gradient.

Elimination and Substitution. The similarity of pH profiles for olefin formation/substitution (Table VI) and the profiles for total product from each cation (Figure 2) indicates that primary, secondary, and tertiary cations show the same response to changes in basicity; hydroxide trapping shows a much larger tendency than water to deprotonate the carbonium ion, producing olefinic products.

The 4,4-Dimethyl-2-pentyl Cation. The free cation was generated by anodic oxidation at pH 14 of potassium 2,4,4-trimethylpentanoate. Although 4,4-dimethyl-2-pentanol and its ester were recognized among the higher boiling products, quantitative analysis was limited to the C_7H_{14} products and the olefins from β cleavage. The radical-disproportionation product 2,2-dimethylpentane could not be resolved from the 4,4-dimethyl-1-pentene fraction; it was assumed to be formed in the same yield as 2,2-dimethylbutane from 2,3,3-trimethylbutanoate oxidation[34] under the same conditions, thus 8% of the C_7 + cleavage products. The olefins from the disproportionation were assigned: 5% 4,4-dimethyl-1-pentene and 3% *trans*-4,4-dimethyl-2-pentene. Substraction of these leaves the olefinic products from 4,4-dimethyl-2-pentyl cation (Table VII).

Table VII. Carbonium Ion Products (Olefins Only) from Electrolyses of Potassium 2,4,4-Trimethylpentanoate[a]

Products	Mole percentages
4,4-Dimethyl-1-pentene	34.3
Propene	19.9
2-Methylpropene	15.5
trans-4,4-Dimethyl-2-pentene	10.7
cis-4,4-Dimethyl-2-pentene	Trace
2,3-Dimethyl-1-pentene	19.6
2,3-Dimethyl-2-pentene	0.0
	100.0

[a] pH 14.

It is apparent that the secondary 4,4-dimethyl-2-pentyl cation reacts as does the primary 3,3-dimethyl-1-butyl; the differences are in accord with the expected consequences of a primary to secondary cation change.

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(37) J. O'M. Bockris, H. Wroblowa, E. Gileadi, and B. J. Piersma, *Trans. Faraday Soc.*, 61, 2531 (1965).

(38) W. T. Grubb and L. W. Niedrach in "Direct Energy Systems," G. Sutton, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 39.

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(40) The encumbered cation of solvolysis does not fragment because electrostatic work of ~70 kcal/mole would be added to the gas-phase reaction heats, making the reaction highly endothermic.[12]

(41) P. Delahay, "Double Layer and Electrode Kinetics," Part I, Interscience Publishers, Inc., New York, N. Y., 1965.

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Table VIII. Electrolyses of Potassium 4,4-Dimethylpentanoate

pH	6.6	8.2	9.4	10.0	13.6	14.0	14.5
M (RCO$_2$K)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amperes	1.0	1.2	1.2	1.4	3.0	3.0	4.0
Volts	15	15	15	15	19	12	8
Voltage at anode *vs.* sce	1.7	1.6	1.6	1.7	1.5	1.9	1.2
Temp, °C	50	45	50	55	65	70	70
Time, min	5	5	7	10	45	80	360
mmoles of RCO$_2$K electrolyzed	4	8	6	8	24	2	6
mmoles of total products	2	1	2	3	12	1	3
mfaradays	3	4	5	9	84	150	900
Current yield, %	120	40	70	60	20	1	1
Products				Mole percentages			
2,2,7,7-Me$_4$-octane	37.9	38.1	38.9	39.7	32.9	7.6	0.8
2,2-Me$_2$-butane	3.4	4.8	5.5	5.5	3.6	2.3	0.7
3,3-Me$_2$-1-butene	5.2	6.8	7.4	7.6	5.5	20.8	24.7
3,3-Me$_2$-1-butanol	15.8	10.1	9.6	10.1	5.9	6.1	8.2
3,3-Me$_2$-1-butyl ester	1.5	1.7	0.8	0.6	1.4	0.5	0.0
Ethene	8.6	11.1	12.4	12.8	20.4	17.2	6.2
2-Me-propene	6.6	9.5	9.9	10.3	13.1	27.3	43.5
2-Me-2-propanol	0.2	0.3	0.2	0.3	1.6	1.4	0.6
2-Me-2-propyl ester	3.2	2.8	1.4	0.8	0.4	0.01	0.0
3,3-Me$_2$-2-butanol	0.4	0.1	0.4	0.5	0.5	0.2	0.3
3,3-Me$_2$-2-butyl ester	0.1	0.2	0.1	0.1	0.0	0.0	0.0
2,3-Me$_2$-1-butene	5.7	6.8	9.2	9.0	8.6	7.7	0.4
2,3-Me$_2$-2-butene	7.8	4.7	1.8	0.07	0.3	1.0	1.4
2,3-Me$_2$-2-butanol	1.4	1.8	1.3	1.7	5.0	1.9	0.0
2,3-Me$_2$-2-butyl ester	1.7	1.2	1.1	0.7	0.2	0.07	0.0
Unidentified compound(s)	0.5	0.0	0.0	0.2	0.6	5.9	13.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The absence of 2,4-dimethyl-1- and -2-pentenes indicates 1,3-methyl shift is not occurring. The greater extent (47 *vs.* 34%) of trapping of unrearranged cation is attributable to two factors: (1) the rearrangement is isoenergetic (secondary → secondary) as opposed to an exothermic rearrangement (primary → secondary) for 3,3-dimethyl-1-butyl cation; (2) the availability of five hydrogens for deprotonation of the 4,4-dimethyl-2-pentyl cation and two for the 3,3-dimethyl-1-butyl cation. A second significant difference is the distribution of the cation between the two routes of β cleavage (24 *vs.* 50%) and double 1,2 shift (23 *vs.* 16%). The origin of this alteration in proportions appears to be a decrease in the rate of β cleavage. The energetics of cleavage of the secondary cation under field-free conditions would preclude it from competition with the other fast reactions. Under the influence of the potential gradient in the vicinity of the anode cleavage becomes feasible from an energetic point of view; however, propylene cleavage is 16 kcal/mole less exothermic than ethylene cleavage (*vide supra*), and therefore slower.

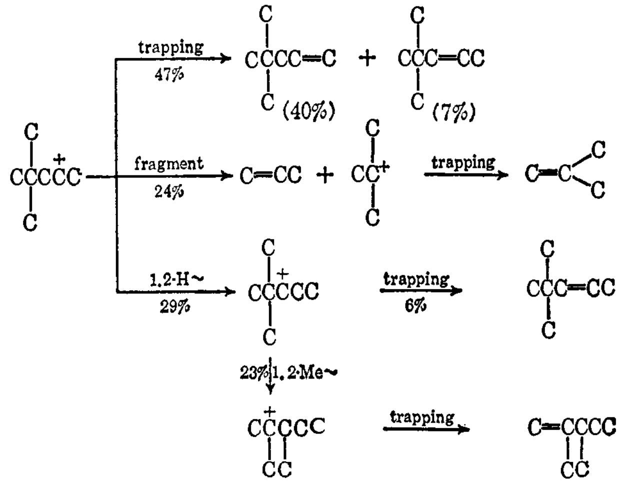

Figure 3. The 4,4-dimethyl-2-pentyl cation generated by anodic oxidation, pH 14; data from Table VII. Partitioning of the 2,2-dimethyl-3-pentyl cation was assumed to be the same as partitioning (between rearrangement and trapping) of the 3,3-dimethyl-2-butyl cation.[34]

The distribution of the 4,4-dimethyl-2-pentyl cation among the olefinic products is summarized in Figure 3.

Free-Radical Products. Among the products obtained from electrolyses of potassium 4,4-dimethylpentanoate are the normal Kolbe products derived from radicals, 2,2,7,7-tetramethyloctane, 2,2-dimethylbutane, and 3,3-dimethyl-1-butene (Table VIII). The excess of 3,3-dimethyl-1-butene over 2,2-dimethylbutane is attributed to the cation route.

The amount of free radical derived products (both coupling and disproportionation) decreases dramatically with increasing alkalinity of the electrolyte; a concommitant increase in carbonium ion products occurs. This is not a new observation;[4,11,43,44] it corroborates the hypothesis that the precursor to the carbonium ion

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Table IX. Electrolyses of Potassium 4,4-Dimethylpentanoate-2-^{14}C

pH	10.0	14.4
M (RCO_2K)	0.2	0.3
Amperes	1.2	4.1
Volts	30	10
Temp, °C	80	75
Time, min	18	105
mmoles of volatile products including CO_2	3.1	1.6
mfaradays	13	270
Current yield, % of volatile products	9	0.1
mCi/mole (RCO_2H)	9.4	8.6

Volatile products	mole %	mCi/ mole	mole %	mCi/ mole
2,2-Dimethylbutane	6.1	17	0.0	..
3,3-Dimethyl-1-butene	12.8	17	43.1	16
Ethene	43.4	17	9.0	14
2-Methylpropene	20.5	0	47.9	0
2,3-Dimethyl-1-butene	17.2	17	0.0	..
	100.0		100.0	

	mmoles	mCi × 10^4	mmoles	mCi × 10^4
Carbon dioxide	2.3	5.4	1.5	43

Table X. Deoxideations of 3,3-Dimethyl-1-butanol

M (KOH)	0.2	0.3	0.8	2.0	3.0	5.0	6.0	8.0	19
Yield, %, of hydrocarbons	0.2	0.4	1.3	1.4	0.8	2.0	10	13	23
Hydrocarbons	Mole percentages								
3,3-Me_2-1-butene	24.8	21.6	27.8	27.5	27.1	47.8	60.2	64.8	72.9
Ethene	45.0	31.5	46.1	48.6	36.0	10.7	5.6	5.4	3.1
2-Me-propene	19.8	32.8	11.6	10.7	15.9	11.3	3.7	4.3	3.2
2,3-Me_2-1-butene	4.0	3.8	3.9	5.8	11.2	23.3	24.1	22.5	18.7
2,3-Me_2-2-butene	6.5	10.3	10.5	7.4	9.8	6.9	6.4	3.0	2.1
Total	100.0	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0

is the free radical. With increasing alkalinity the partial current density increases for discharge of oxygen and decreases for discharge of carboxylates. At high alkalinities the rate of radical production and the instantaneous radical concentration are smaller. Coupling and disproportionation have $[R\cdot]^2$ dependence whereas cation formation has $[R\cdot]^1$. It is well established that dimer yields improve with increasing current density[4,43-46] under conditions where carboxylate is the sole electroactive species.

The disproportionation to coupling ratio for the 3,3-dimethyl-1-butyl radical is 0.1. It is perhaps fortuitous that the gas-phase values for ethyl and 1-propyl radicals are also 0.1,[47] since there is good reason to believe that the Kolbe bimolecular radical reactions often occur on the electrode surface.[48-50]

Experimental Section

4,4-Dimethylpentanoic acid was prepared in 90% yield by carbonation of the Grignard reagent from 1-chloro-3,3-dimethylbutane; bp 95° (6.5 mm); $n^{25}D$ 1.4195; nmr: singlet (9 H) at 0.90 ppm, triplet with second-order splitting (2 H) at 1.49 ppm, triplet with second-order splitting (2 H) at 2.26 ppm, and singlet (1 H) at 12.26 ppm.

Electrolyses of potassium 4,4-dimethylpentanoate were carried out in the apparatus previously described,[51] a slow sweep of N_2 through the anode compartment removing the volatile products to traps. Less volatile products were extracted from the electrolyte. Products were separated by gas chromatography and identified by comparison of retention times, infrared spectra, and mass spectra with authentic samples. Unused acid was removed by acidification and extraction, with titration for determining the amount. All gas chromatographic data were converted to mole percentages with the appropriate empirical thermal responses. The results are summarized in Table VIII. The esters were 4,4-dimethylpentanoates. In addition, oxygen, carbon dioxide, and small amounts of 2-methyl-1-butene and 3,3-dimethylbutanal were produced; hydrogen was the only recognizable cathodic product.

The composition of the volatile products was studied as a function of time and found to be invariant over the entire electrolysis period.

4,4-Dimethylpentanoic-2-^{14}C Acid. This acid was prepared in the same manner as above, starting with 1-bromo-3,3-dimethylbutane-1-^{14}C (~0.034 mole)

$$\mathrm{Me_3CCH_2MgCl} \xrightarrow{^{14}\mathrm{CO_2}} \mathrm{Me_3CCH_2{}^{14}CO_2H} \xrightarrow{\mathrm{LiAlH_4}}$$

$$\mathrm{Me_3CCH_2{}^{14}CH_2OH} \xrightarrow{\mathrm{Ph_3PBr_2}} \mathrm{Me_3CCH_2{}^{14}CH_2Br}$$

giving the desired acid, 8.61 mCi/mole, ir identical with nonradioactive acid. Radioactivity assay was as follows: vpc effluent was led from the thermal conductivity detector into a flow-through ion chamber (Cary Model 5010), scavenged by a flow of argon ten times greater than the vpc flow; current was measured by a vibrating reed electrometer (Cary Model 31) and simultaneously recorded with the thermal conductivity vpc trace. The absolute ^{14}C values were obtained by comparison with a commercial standard toluene-^{14}C sample (New England Nuclear Corp.). With the usual corrections the two traces yielded molar percentages.

Electrolyses of Potassium 4,4-Dimethylpentanoate-2-^{14}C. The technique was the same as that described above for electrolyses of potassium 4,4-dimethylpentanoate except that at the end of an experiment the electrolyte was acidified (H_2SO_4) to a Congo red end point, and the carbon dioxide released was collected with the volatile products; the results of two experiments are given in Table IX. The less volatile products were not analyzed.

3,3-Dimethyl-1-butanol. Hydroboration[52] of 3,3-dimethyl-1-butene gave 3,3-dimethyl-1-butanol in 59% yield, bp 141-143° (730 mm), 94.2% pure (contaminants: 1.0% 3,3-dimethyl-2-butanol and 4.8% of four other components), lit.[53] bp 139-140° (727 mm).

Deoxideations of 3,3-dimethyl-1-butanol were carried out by stirring 100 ml of aqueous potassium hydroxide solution with 1.0 g of alcohol, and adding slowly 7.6 g of bromoform while the flask was heated in a 150° oil bath. The volatile products were swept out in a nitrogen gas stream and analyzed as above; see Table X.

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Table XI. Electrolysis of Potassium 2,4,4-Trimethylpentanoate

pH	14.0
RCO_2K, *M*	1.0
Amperes	8.0
Volts	13.0
Voltage at anode *vs.* sce	1.2
Temp, °C	55
Time, min	40
mmoles of RCO_2K electrolyzed	19
mmoles of volatile products	6
mfaradays	200
Current yield, %, of volatile products	5

Volatile products	Mole %
2,2-Dimethylpentane 4,4-Dimethyl-1-pentene	40.6[a]
Propene	17.2
2-Methylpropene	13.4
trans-4,4-Dimethyl-2-pentene	12.0
cis-4,4-Dimethyl-2-pentene	Trace
2,3-Dimethyl-1-pentene	16.9
2,3-Dimethyl-2-pentene	0.0
	100.0

[a] Unresolved on the vpc column.

3,3-Dimethyl-1-butyl *p*-Toluenesulfonate. This ester was prepared in 84% yield by allowing 3,3-dimethyl-1-butanol (10.2 g, 0.10 mole) containing 1% 3,3-dimethyl-2-butanol to react with *p*-toluenesulfonyl chloride (21.0 g, 0.15 mole) and pyridine (60 cc). The crude tosylate was taken up in chloroform and then washed successively with dilute HCl, water, dilute K_2CO_3, and water; the chloroform solution was then dried over anhydrous K_2CO_3, and the chloroform was removed at 30° under reduced pressure; nmr: singlet (9.0 H) at 0.86 ppm, triplet (2.1 H) at 1.55 ppm, singlet (3.3 H) at 2.41 ppm with a small shoulder on the downfield side (possibly some *o*-tosylate), triplet (2.0 H) at 4.07 ppm, poorly shaped doublet (2.3 H) centered at 7.31 ppm, poorly shaped doublet (2.3 H) centered at 7.75 ppm. There was a small peak (*ca.* 0.17 H) at 1.18 ppm; this latter peak indicates the possible presence of ~5% 3,3-dimethyl-2-butyl tosylate or ~3% 2,3-dimethyl-2-butyl tosylate.

Solvolyses of 3,3-dimethyl-1-butyl *p*-Toluenesulfonate were carried out by refluxing the ester for 19 hr in acetic or formic acids in the presence of a small excess of sodium acetate or cesium formate, respectively. Esters were isolated in 50–60% yield. After reduction with lithium aluminum hydride, the alcohol component was identified by gas chromatographic retention time as 3,3-dimethyl-1-butanol, not contaminated by any other C_6 alcohol. In another acetolysis the olefinic products were removed by sweeping the reaction vessel with nitrogen during the solvolysis, the last traces being removed by distilling at 10 mm three-quarters of the solvent into the trap. The olefinic products and yields were: 1.4% 3,3-dimethyl-1-butene, 0.9% 2,3-dimethyl-1-butene, and 1.0% 2,3-dimethyl-2-butene; ethylene and isobutylene were not detected.

2,4,4-Trimethylpentanoic Acid. The Grignard reagent from 2-chloro-4,4-dimethylpentane, (bp[54] 64.5° (85 mm), $n^{20}\mathrm{D}$ 1.4180, 99% pure by vpc, 74.8 g, 0.556 mole) and magnesium turnings was carbonated with CO_2, yielding 2,4,4-trimethylpentanoic acid (35%), bp 108–110° (12 mm), $n^{25}\mathrm{D}$ 1.4231; lit.[55] bp 109.8–109.5° (12–14 mm), $n^{20}\mathrm{D}$ 1.4231.

Electrolysis of Potassium 2,4,4-Trimethylpentanoate. The electrolysis cell[51] was modified to separate the cathode and anode by a sintered-glass disk of medium porosity; the cathode compartment contained 12 *M* KOH, the anode compartment the aqueous RCO_2K-KOH electrolyte. In addition to the compounds listed in Table XI, 4,4-dimethyl-2-pentanol and 4,4-dimethyl-2-pentyl 2,4,4-trimethylpentanoate were identified; the remainder, probably rearranged alcohols and esters, were not identified.

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Conformational Stability in Ethyl 2,3-Dibromopropionate

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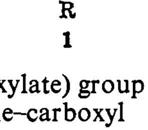
Abstract: Preparation of *threo*-$BrCHDCDBrCO_2C_2H_5$ and comparison of its nmr spectrum with that of undeuterated ester permits unequivocal identification of the most stable conformer as the one with *trans* bromines.

A study of the conformer distribution in two 1-substituted 1,2-dibromoethanes, $BrCH_2CHBrR$, has shown[2] that the more stable conformer with R = *t*-butyl is **1** (bromines *gauche*) whereas that with R = C_6H_5 is **2** (bromines *trans*). It has been assumed[3] that the most stable conformer of $BrCH_2CHBrCO_2H$ (R = CO_2H) corresponds to **2**, but no definitive support is available. Although dipole–dipole repulsions between bromines will undoubtedly favor **2**, the carboxyl (and carboxylate) group is also a polar one. The extent of bromine–carboxyl (or carboxylate) electrostatic interactions will depend sensitively on the precise geometry of the latter with respect to the halogen, but it seems reasonable that these will be repulsive and will tend to favor **1**.



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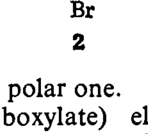

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The conformation of ethyl 2,3-dibromopropionate has been unequivocally determined by examination of

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(1) This investigation was supported in part by Public Health Service Research Grant GM-12113 from the National Institute of General Medical Sciences.

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