sociated with a *trans*-disubstituted double bond. The mass spectra of the isomers are identical with parent peaks at m/e 132.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.39; H, 8.96.

Photostationary State. Purified 1-phenyl-2-butene (50 to 150 mg, 3.8×10^{-4} to 1.1×10^{-3} mol) was dissolved in 150 ml of spectral grade cyclopentane contained in a water-jacketed cylindrical Pyrex vessel. A quartz immersion well, containing a mercury resonance lamp, was placed into the photolysis vessel. The solution was deaerated with argon for about 1.5 hr before beginning the irradiation. Throughout the irradiation period the photolysis vessel was maintained at $25.0 \pm 0.1°$ using a Bronwill Constant Temperature Circulator. After a photostationary state was obtained, as observed by periodic analysis of aliquots, the solution was analyzed and the ratio of the two isomers obtained.

Quantum Yields. Purified *cis*- and/or *trans*-1-phenyl-2-butene (130 mg, 9.8×10^{-4} mol) was added to 50 ml of spectral grade cyclopentane contained in Vycor glass tubes and deaerated for about 1.5 hr by bubbling argon through the solutions. Irradiation was supplied by the mercury resonance lamp using a rotating turntable (*cf.* Quenching Experiments). After the irradiation was complete, a known weight of internal standard was added, and the amount of the desired isomer of 1-phenyl-2-butene formed was determined. In each determination, the amount of product formed was corrected for back reaction by the method of Lamola.[23] In all quantum yield experiments no loss of 1-phenyl-2-butene was observed. The light intensity was determined during the irradiation of the 1-phenyl-2-butene solution by uranyl oxalate actinometry.

Quenching Experiments. Eight Vycor glass tubes (2.4 cm o.d. and 18.5 cm long) were filled with 50 ml of spectral grade cyclopentane and about 25 mg (1.89×10^{-4} mol) of purified *trans*-1-phenyl-2-butene. In the *trans*-2-hexene quenching experiments, varying amounts (0.17 to 1.09 g, 2.1×10^{-3} to 1.3×10^{-2} mol) of

trans-2-hexene were added to six of the tubes. In the *cis*-piperylene experiments varying amounts (7.3 to 61 mg, 1.1×10^{-4} to 9.0×10^{-4} mol) of *cis*-piperylene were similarly added to six tubes. In both of the quenching studies two of the tubes served as standards with zero quencher concentration. The sample tubes were deaerated for at least 1 hr with argon after which time they were placed in a rotating turntable apparatus approximately equidistant from each other and approximately equidistant (4.0 cm) from a centrally located mercury resonance lamp situated in a quartz immersion well. The entire system, contained in a water-filled glass vessel, was maintained at $25.0 \pm 0.2°$ using a Bronwill Constant Temperature Circulator. The turntable apparatus was constructed so that the tubes could be rotated around the centrally located lamp during irradiation. After allowing the tubes to come to thermal equilibrium with the bath, the samples were irradiated, and after irradiation a known weight of internal standard was added to each tube and the amount of *cis*-1-phenyl-2-butene formed was determined. The amount of the *cis* isomer formed was corrected for back reaction as previously mentioned and, in the piperylene experiments, correction was made for the amount of light absorbed by the *cis*-piperylene. When using *trans*-2-hexene as quencher no loss of 1-phenyl-2-butene was observed. In the *cis*-piperylene quenching experiments, 1-phenyl-2-butene was shown not to have disappeared except in the three samples which contained *cis*-piperylene in concentrations greater than 1.2×10^{-2} M. In these three samples the loss of 1-phenyl-2-butene was 1.5% or less.

Light Sources. For the photostationary state and quantum yield determinations a Hanovia low-pressure, mercury resonance lamp emitting at only 253.7 mμ was employed. The lamp itself was made from Vycor glass to remove the 184.9-mμ mercury resonance line.

Intermediates in Anodic Oxidation of Carboxylates. Chronopotentiometry

Paul H. Reichenbacher,[1] Michael D. Morris, and Philip S. Skell

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received October 4, 1967

Abstract: Two steps are observed in chronopotentiometric oxidations of cesium salts of 2,2-dimethylpropanoic and 2,2-dimethylpentanoic acids on a platinum electrode in acetonitrile. The first step is a diffusion-controlled, one-electron oxidation; the second is not diffusion controlled and indicates that the product of the first step is partially lost in reactions not involving electrochemical oxidation. Acids less substituted on the 2 position show similar but less reproducible behavior.

The electrolysis of carboxylates is generally assumed to involve the intermediacy of both free radicals and in some cases carbonium ions.[2-11] The exact nature

of the initial carboxylate–anode process, however, is not well understood.[12] The transient existence of alkyl carboxylate radicals ($RCO_2\cdot$) has generally been ac-

$$RCO_2^- \text{ (solution)} \longrightarrow RCO_2\cdot \text{ (adsorbed)} + e^- \longrightarrow$$

$$R\cdot \text{ (adsorbed)} + CO_2 \quad (1)$$

cepted despite the fact that alkyl carboxylate radicals from chemical processes have very short lifetimes (10^{-9} to 10^{-10} sec).[13] Most chemists concerned with anodic oxidation of carboxylates have assumed or have offered varying degrees of evidence that $RCO_2\cdot$ produced

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

(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 581.

(3) E. J. Corey, R. R. Sauers, and S. S. Swann, *J. Am. Chem. Soc.*, **79**, 5826 (1957); E. J. Corey and R. R. Sauers, *ibid.*, **81**, 1743 (1959).

(4) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, and E. T. Kaiser, *ibid.*, **82**, 2645 (1960).

(5) N. L. Bauld, Ph.D. Thesis, University of Illinois, 1959.

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(7) L. Eberson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963).

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(10) J. G. Traynham and J. S. Dehn, *ibid.*, **89**, 2139 (1967).

(11) 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.

(12) B. E. Conway and M. Dzieciuch, *Can. J. Chem.*, **41**, 22, 38, 55 (1963).

(13) W. Braun, L. Rajkenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

anodically is adsorbed on the electrode surface and exists longer than a nonadsorbed $RCO_2 \cdot$ species;[12,14-18] eq 1 represents the over-all electron transfer and decarboxylation reaction of the classical Kolbe electrolysis. Eberson,[7] on the other hand, takes the short lifetime of the chemically generated (nonadsorbed) carboxylate radical as support for his theoretical argument (based on thermodynamics) that electrolyses of carboxylate anions proceed with concerted electron transfer and loss of carbon dioxide (eq 2).[19] Conway and

$$RCO_2^- \longrightarrow R \cdot + CO_2 + e^- \qquad (2)$$
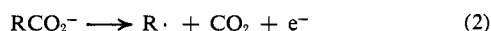
Vijh[22] have criticized Eberson's paper[7] for not considering adsorbed species for which his calculations based on free species are not relevant. Further, loss of electron from carboxylate to anode is expected to be fast compared with nuclear motion,[23] and while some loosening of the $R-CO_2$ bond may be prerequisite to electron transfer (see papers by Marcus[24,25]), loss of CO_2 cannot be as rapid as the vertical transition of electron transfer.

Most theoretical studies of the anodic oxidation of carboxylates have been concerned with the details of the over-all reaction 1, for which the final product is usually the hydrocarbon $R-R$ and radical disproportionation products. However, in certain systems the carbonium ion R^+ is formed by further oxidation of the radical, reaction 3. Carbonium ion intermediacy has

$$R \cdot \longrightarrow R^+ + e^- \qquad (3)$$
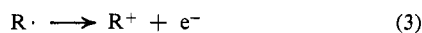
been deduced by comparison of the products (olefins, alcohols, esters, often with rearranged skeletons) from anodic oxidations of carboxylates and the products from better understood chemical reactions leading to carbonium ions.[6,9] That the carbonium ion precursor is the radical can be inferred from the decrease in the relative amount of radical dimer and the accompanying increase in the relative amount of carbonium ion products as R is varied from primary to secondary to tertiary. This occurs because the ionization potentials of radicals decrease sharply in the order primary > secondary > tertiary.

$$R \cdot \longrightarrow R^+ + e^- \text{ (gas phase)}[26]$$

R	Ionization potential, kcal/mol
methyl	229
1-butyl	199
2-butyl	183
t-butyl	171

Low current densities and alkaline electrolytes (more O_2 production and less carboxylate oxidation) promote carbonium ion formation[2,14,27] by decreasing the concentration of adsorbed alkyl radicals; the lowered concentration of radicals has a larger effect in diminishing the products from bimolecular radical reactions, coupling and disproportionation (eq 4), than the carbonium ion products which have a unimolecular dependence on radical concentration (eq 5).

$$\left.\begin{array}{l} 2R \cdot \longrightarrow R-R \\ \\ 2R \cdot \longrightarrow \text{alkene} + \text{alkane} \end{array}\right\} \quad \text{rate} = k[R \cdot]^2 \quad (4)$$

$$R \cdot \longrightarrow R^+ + e^- \qquad \text{rate} = k[R \cdot] \qquad (5)$$

The anodic oxidations of cesium 2,2-dimethylpropanoate and cesium 2,2-dimethylpentanoate, in which carbonium ion formation dominates in aqueous electrolyses,[28] have been examined under chronopotentiometric conditions[29,30] to verify the postulated two-step processes. The oxidations were studied in acetonitrile both to avoid the complications of water oxidation and to provide a medium in which the cesium carboxylates and the products are soluble.

Experimental Section

Reagents. Cesium oxide was prepared by careful air oxidation of cesium metal (MSA Research Corp., Callery, Pa.). The oxide was dissolved in distilled water and used to neutralize portions of 2,2-dimethylpropanoic acid and 2,2-dimethylpentanoic acid. The water was evaporated under vacuum from the cesium carboxylates so obtained and the salts were recrystallized from hot chlorobenzene.

Acetonitrile (bp 81.4-81.8°, 0.3% water) was chromatographed over activated alumina and then refluxed over P_2O_5 for 2 hr. This acetonitrile was then distilled from the P_2O_5 (4 ft × 1 in. metal-packed column, bp 80.4° (730 mm)) onto CaH_2 while a N_2 atmosphere was maintained in the system. After refluxing the acetonitrile over CaH_2 (N_2 atmosphere) for 2 hr, it was distilled (as above) into a dry 1-l. flask with a bottom outlet; the grease used on the stopcock was Spectro-Vac stopcock grease (Robert R. Austin, Pasadena, Calif.); it does not dissolve in acetonitrile. The purified acetonitrile was kept and dispensed in a drybox (N_2 atmosphere, P_2O_5 desiccant).

Tetrapropylammonium tetrafluoroborate (Ozark-Mahoning Co., Tulsa, Okla.) was recrystallized from a hot methanol-ether solution[31] to give white needles; these were dried in a rotary evaporator (10 hr, 3 mm, 25°). The dried tetrapropylammonium tetrafluoroborate (mp 244.0-244.5°) was stored in the drybox.

Apparatus. The chronopotentiometric circuitry used was conventional.[29,30] The constant current source consisted of several "B" batteries (180 V) in series with an appropriate dropping resistor. Chronopotentiometric curves were recorded with a Leeds and Northrup Speedomax recorder (0.8-sec, full-scale deflection). A cathode follower (Heath EUW-19 operational amplifier) was placed between the working-reference electrode pair and the recorder to prevent the measuring system from drawing significant currents from the electrolysis system.

(14) B. E. Conway, "Theory and Principles of Electrode Processes," The Ronald Press, New York, N. Y., 1965, pp 136, 166 ff, and 244 ff.

(15) B. E. Conway, E. Gileadi, and M. Dzieciuch, *Electrochim. Acta*, **8**, 143 (1963).

(16) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); B. C. L. Weedon, *Advan. Org. Chem.*, **1**, 1 (1960).

(17) T. Dickinson and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **58**, 382, 388, 400 (1962).

(18) C. W. Fleishmann, G. K. Johnson, and A. T. Kuhn, *J. Electrochem. Soc.*, **111**, 602 (1964).

(19) To the extent that cobaltic oxidation of carboxylate parallels anodic oxidation of carboxylate, work by Clifford and Waters[20] corroborates Eberson's suggestion. See also ref 21.

(20) A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 2796 (1965).
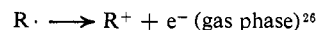
(21) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Part A, Academic Press Inc., New York, N. Y., 1965, pp 180-182, 228-235, 264-266, and 293-301.

(22) B. E. Conway and A. K. Vijh, *Electrochim. Acta*, **12**, 102 (1967).

(23) E. Sacher and K. J. Laidler in "Modern Aspects of Electrochemistry," No. 3, J. O'M. Bockris and B. E. Conway, Ed., Butterworth & Co., Washington, D. C., 1964, p 8.
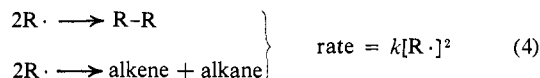
(24) R. A. Marcus in "Transactions of the Symposium on Electrode Processes," E. Yeager, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 239.

(25) R. A. Marcus, *J. Phys. Chem.*, **67**, 853, 2889 (1963); also later papers in *J. Phys. Chem.* and *J. Chem. Phys.*

(26) F. P. Lossing, P. Kebarle, and J. B. de Sousa, *Advan. Mass Spectrometry, Proc. Conf. Univ. London*, **1**, 431 (1959).

(27) H. Hofer and M. Moest, *Ann.*, **323**, 284 (1902).

(28) P. S. Skell, R. J. Maxwell, J. T. Keating, and P. H. Reichenbacher, unpublished results.

(29) D. G. Peters in "Standard Methods of Chemical Analysis," Vol. III, Part A, F. J. Welcher, Ed., 6th ed, D. van Nostrand Co., Princeton, N. J., 1966, pp 404-427.

(30) D. G. Davis in "Electroanalytical Chemistry," Vol. I, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 157-196.

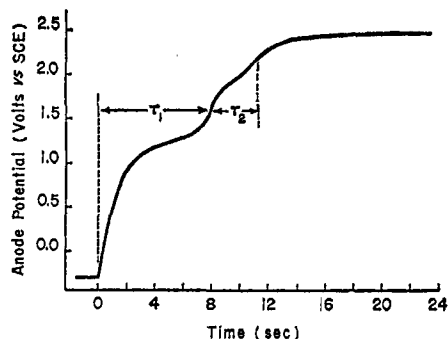(31) C. M. Wheeler, Jr., and R. A. Sandstedt, *J. Am. Chem. Soc.*, **77**, 2024 (1955).

Figure 1. Chronopotentiogram for oxidation of cesium 2,2-dimethylpropanoate (0.00620 M); the supporting electrolyte was tetrapropylammonium tetrafluoroborate (0.2 M) in acetonitrile. The Pt wire anode area was 0.28 cm²; the electrolysis current was 234 μA; transition times (τ) measured according to the method of Kuwana.[33]

The electrolysis cell was a Pyrex container, 4.5 cm diameter by 10.5 cm high. The auxiliary cathode was three coils (3.8 cm diameter) of no. 16 platinum wire. The working anode was a piece of no. 16 platinum wire sealed in a soft glass tube (0.7 cm o.d.); there was a soft glass bead sealed over the tip of the anode leaving a 0.63 cm length of exposed platinum wire (0.14 cm diameter); the surface area was 0.28 cm². The reference electrode was a saturated calomel electrode (sce) connected to the electrolysis cell according to the method of Kolthoff and Coetzee[32] by an aqueous saturated KCl bridge.

Technique. A stock solution of tetrapropylammonium tetrafluoroborate (0.2 M) in acetonitrile was compounded in the drybox and stored there in a stoppered bottle. The dry chronopotentiometric cell was placed in the drybox overnight; the cell was then filled with electrolyte (50 cc in the cell proper; 3 cc in the salt bridge compartment[32]). The cell was removed from the drybox and was connected to the electrolysis circuit. Chronopotentiograms were recorded making certain beforehand that the cell mounting assembly was motionless and vibration free. Between chronopotentiograms the electrolyte was stirred and the anode was made cathodic by reversing positive and negative leads. Currents varying from 30 to 6900 μA were used; these currents were determined by measuring (null potentiometer) the potential across a precision resistor in series with the working circuit. The cesium carboxylate to be electrolyzed (kept in the drybox) was placed in a closed weighing bottle and removed from the drybox and weighed; a quantity of cesium carboxylate was quickly added to the electrolysis cell (but not to the salt bridge compartment), and the weighing bottle was weighed again. Cesium carboxylate concentrations of 0.001 to 0.006 M were so obtained. Chronopotentiograms were then obtained from the RCO₂Cs–Pr₄NBF₄ solution. The transition times (τ_1 and τ_2) were measured according to the method of Kuwana,[33] and the potential (E vs. sce) was noted at $\tau_1/4$ and $\tau_2/4$.

Results

A chronopotentiogram of 6.02 $\times$ 10⁻³ M cesium 2,2-dimethylpropanoate in 0.2 M tetrapropylammonium tetrafluoroborate supporting electrolyte is shown as Figure 1. Similar chronopotentiograms were obtained for cesium 2,2-dimethylpentanoate. The distinctive feature of the chronopotentiometry of these systems is the presence of two-step waves. Previous reports[34,35] mention only one anodic wave, a one-electron oxidation, presumably reaction 1.

The data are summarized in Table I. The first waves of both carboxylates obey the Sand equation[29,30,36] as

(32) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem Soc.*, **79**, 870 (1957).
(33) Attributed to T. Kuwana by C. D. Russell and J. M. Peterson, *J. Electroanal. Chem.*, **5**, 467 (1963).
(34) D. H. Geske, *ibid.*, **1**, 502 (1960).
(35) D. H. Geske, Department of Chemistry, Cornell University, letter to P. S. Skell, Department of Chemistry, The Pennsylvania State University, Feb 10, 1965.
(36) H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

modified by Peters and Lingane[37] for cylindrical diffusion (*i.e.*, a wire electrode), but in both cases the second transition times are too short to be caused by a diffusion-controlled process. Furthermore, the ratio τ_2/τ_1 decreases strongly with increasing first transition time. For planar diffusion this ratio is constant for diffusion-controlled processes;[29,30] for cylindrical diffusion the ratio increases slowly with increasing first transition time.[37]

Table I. Chronopotentiometry of Cesium Carboxylates in Acetonitrile[a,b]

c	i	τ_1	τ_2	τ_2/τ_1	$E_{1/4}^{(1)}$	$E_{1/4}^{(2)}$	$i\tau_1^{1/2}/$ Ac
Cesium 2,2-Dimethylpropanoate							
6.20	125	32.4	10.2	0.31	1.10	1.86	350
6.20	134	26.8	9.5	0.35	1.08	1.88	350
6.20	144	21.8	8.4	0.39	1.07	1.87	340
6.20	150	20.8	8.9	0.43	1.07	1.86	350
6.20	164	16.3	6.5	0.40	1.04	1.86	340
6.20	170	15.2	5.8	0.38	1.04	1.85	340
6.20	179	13.5	5.4	0.40	1.01	1.83	340
6.20	187	12.2	5.0	0.41	0.99	1.84	340
6.20	208	9.9	4.2	0.42	0.95	1.84	340
6.20	234	8.0	3.4	0.43	0.88	1.82	350
6.20	268	6.0	2.9	0.48	0.79	1.78	350
6.20	353	3.6	2.0	0.56	0.60	1.73	360
6.20	379	3.2	1.8	0.56	0.57	1.71	370
				Av	0.94	1.83	350
					±0.14	±0.04	±10
Cesium 2,2-Dimethylpentanoate							
1.80	46	18.1	13.0	0.72	0.86	1.71	350
1.80	52	15.5	13.4	0.86	0.79	1.72	370
1.80	56	13.1	14.7	1.1	0.82	1.72	370
1.80	61	10.8	8.0	0.74	0.75	1.69	370
1.80	73	8.0	5.9	0.74	0.70	1.68	380
3.10	91	18.0	12.2	0.68	0.97	1.75	400
3.10	100	12.9	8.3	0.64	0.87	1.75	380
3.10	106	10.9	6.4	0.59	0.84	1.76	370
3.10	113	11.8	7.6	0.64	0.89	1.75	410
3.10	120	8.7	4.9	0.56	0.81	1.70	380
				Av	0.83	1.72	380
					±0.06	±0.02	±10

[a] Legend: c = concentration of cesium carboxylate (mmoles/liter); i = constant electrolysis current (microamperes); τ_1 = transition time (seconds) of first wave measured according to the method of Kuwana;[33] τ_2 = transition time (seconds) of second wave measured from the end of the first wave according to Kuwana; τ_2/τ_1 = ratio of transition times (unitless), see text for significance; $E_{1/4}^{(1)}$ = the quarter-wave potential (volts vs. sce) measured at $\tau_1/4$; $E_{1/4}^{(2)}$ = the quarter-wave potential (volts vs. sce) measured at $\tau_2/4$; $i\tau_1^{1/2}/Ac$ = (amp cm sec$^{1/2}$ mole⁻¹), corrected to linear diffusion with Evans and Price table (D. H. Evans and J. E. Price, *J. Electroanal. Chem.*, **5**, 77 (1963)), diffusion coefficients of Table II employed for this correction. [b] Before electrolyzing cesium carboxylate, chronopotentiograms of the solvent–electrolyte system (acetonitrile, 0.2 M tetrapropylammonium tetrafluoroborate) were obtained. In 50% of the blank runs no chronopotentiometric wave was observed; in the rest a single wave was noted: $E_{1/4}$ = 2.49 ± 0.07 V; $i\tau^{1/2}$ was constant (±3%) for different values of i for the same experiment, but $i\tau^{1/2}$ varied from 1.1 to 4.9 mA sec$^{1/2}$ depending on the experiment.

Conclusions

The First Wave. There are no independent diffusion coefficient data for 2,2-dimethylpropanoate and 2,2-dimethylpentanoate in acetonitrile. However, the aqueous diffusion coefficient has been measured[38] for

(37) D. G. Peters and J. J. Lingane, *J. Electroanal. Chem.*, **2**, 1, 249 (1961).
(38) W. J. Albery, A. R. Greenwood, and R. F. Kibble, *Trans. Faraday Soc.*, **63**, 360 (1967).

the former carboxylate and can be calculated[38] for the latter. These data can be converted via the Stokes–Einstein equation[39] into acetonitrile diffusion coefficients. With these approximate values of the diffusion coefficients (Table II) estimates of the n values of the first waves can be obtained from the transition time data; the data are fitted to the Peters and Lingane equation[37] by use of the Evans and Price table.[40] Table II summarizes the n value estimates for the two carboxylates. In both cases the n value is unity within experimental error. Thus, the first step of each chronopotentiometric wave is a one-electron oxidation to carboxylate radical and/or its decomposition products $(R \cdot + CO_2)$.

Table II. The First Chronopotentiometric Wave

Cesium carboxylate	$n^2D \times 10^{5\,a}$	$D \times 10^5$	n
2,2-Dimethylpropanoate	1.77 ± 0.07	2.20^b	0.90
2,2-Dimethylpentanoate	2.06 ± 0.14	1.77^c	1.1

a Calculated from the data of Table I using the Sand equation[29,30,36] as modified by Peters and Lingane[37] for cylindrical diffusion. *b* Diffusion coefficient (cm²/sec) in acetonitrile calculated from the diffusion coefficient in water by the Stokes–Einstein equation[39] (viscosities at 25° used [E. C. Bingham and R. F. Jackson, *Bull. Natl. Bur. Std.*, **14**, 75 (1918)]). The diffusion coefficient in water was taken from Albery, Greenwood, and Kibble.[38] *c* Same as footnote *b*, except that the diffusion coefficient in water was calculated from an equation by Albery, Greenwood, and Kibble;[38] the molecular volume needed was obtained by the method of Le Bas: G. Le Bas, "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green, and Co., London, 1915; D. E. Bidstrup and C. J. Geankoplis, *J. Chem. Eng. Data*, **8**, 170 (1963); R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 51.

The Second Wave. The second chronopotentiometric waves are not diffusion controlled as shown by the behavior of the ratio τ_2/τ_1. If the electrochemical steps had been successive ones, $A \rightarrow B + e$ and $B \rightarrow C + e$, without other reactions utilizing B, the two steps of the oxidation waves would have been related[29,30] by $\tau_2 = 3\tau_1$ (after correction to linear diffusion). If consumption of B is so rapid that no oxidation of B to C occurs, but if direct two-electron oxidation of A to C takes place, then the expected[41] transition time ratio (corrected to linear diffusion) is $\tau_2 = \tau_1$. The fact that $\tau_1 > \tau_2$ implies that the second electron transfer is coupled to a preceding or concurrent chemical side reaction and that direct two-electron oxidation of carboxylate does not occur. The only reasonable possibility for the second electron transfer step is the further one-electron oxidation of an alkyl radical, eq 3. However, alkyl radicals react with one another, even if electrode adsorbed. Thus, the second transition time is much shorter than predicted for diffusion control. The fraction of the electrogenerated radical consumed by dimerization increases with the time of the experiment (i.e., the first transition time), so that the ratio τ_1/τ_2 decreases with increasing first transition time.[42,43]

Mathematical complexity precludes the exact treatment of this case in which the dissipating reaction is higher than first order in the intermediate.[44]

One-electron oxidation of carboxylate continues after the first transition time, whether or not the initially formed carboxylate radicals are lost by side reactions.[41] For this reason, and because adsorbed alkyl radicals are rapidly dimerized to soluble alkanes, there is no fixed quantity of alkyl on the electrode surface to undergo further oxidation. Consequently, the second transition time must be determined not by the time required to oxidize a constant quantity of adsorbed material but by the relative rates of dimerization and further oxidation.

Other Carboxylates. The chronopotentiometries of the cesium salts of the following carboxylic acids have been investigated: propanoic, 2-methylpropanoic, hexanoic, 2-methylpentanoic, and octanoic acids. In each case a diffusion-controlled first wave ($n = 1.0 \pm 0.1$) corresponding to reaction 1 was observed. For each carboxylate second waves were observed, but the reproducibility was poor and from time to time it was impossible to obtain second waves with any of these carboxylates. It is well known that anodic processes are quite sensitive to the state of the electrode (see, for example, ref 12, 29, 30, and 45), and it is likely that the electrode is easily and irreproducibly deactivated toward oxidation of the more difficultly oxidizable primary and secondary alkyl radicals[26] despite efforts to maintain a reproducible history for the electrode between chronopotentiometric experiments. Details of this work may be found elsewhere.[46]

Summary

This work demonstrated that electrolysis of cesium carboxylates in acetonitrile involves two discrete electrooxidations and a chemical reaction competing with the second electrooxidation. The first step was shown to be a one-electron process. These results are consistent with the following scheme.
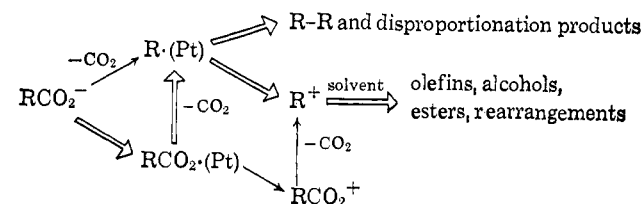
However, other results implicate the heavy arrows, eliminating the light ones as important pathways.

(1) The relative rates of discharge of carboxylates[47] are independent of the primary, secondary, or tertiary structure of R, thus precluding the one-step $RCO_2^- \rightarrow e + R \cdot (Pt) + CO_2$.

(2) Chemical intuition suggests that if anodic oxidation of carboxylates leads to RCO_2^+, it would generate a R^+ species which would show behavior identical with R^+ from RN_2^+ decompositions; this is not observed. Decompositions of alkyldiazonium ions and anodic oxidations of carboxylates with R = bicyclooctyl show

(39) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1952, p 97.
(40) See Evans and Price, Table I, footnote *a*.
(41) D. H. Evans, *J. Electroanal. Chem.*, **9**, 267 (1965).
(42) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).
(43) D. H. Evans, *ibid.*, **36**, 2027 (1964).

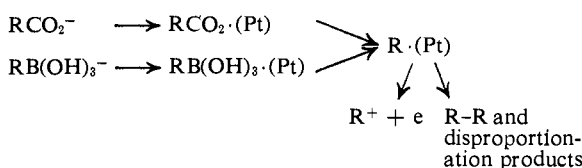(44) S. W. Feldberg and C. Auerbach, *ibid.*, **36**, 505 (1964).
(45) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers Inc., New York, N. Y., 1965.
(46) P. H. Reichenbacher, Ph.D. Thesis, The Pennsylvania State University, 1967.
(47) P. H. Reichenbacher, M. Y.-C. Liu, and P. S. Skell, *J. Am. Chem. Soc.*, **90**, 1816 (1968).

marked differences in the behavior of the carbonium ions.[48]

(3) Anodic oxidations of alkaneboronates and the corresponding carboxylates result in strikingly similar products (both free-radical and carbonium ion products) and product distributions,[49,50] suggesting similar intermediates and similar product-forming paths.[11]

$$RCO_2^- \longrightarrow RCO_2 \cdot (Pt)$$
$$RB(OH)_3^- \longrightarrow RB(OH)_3 \cdot (Pt)$$

$$\Rightarrow R \cdot (Pt)$$

$$R^+ + e \quad R-R \text{ and disproportion-ation products}$$

(4) Adsorbed carboxylate radicals are implicated by the observation that 60-cycle alternating current results in less than 1% of the reaction which would be obtained by application of direct current in the same set-up.[51,52] Each electrode is anodic 0.008 sec and then

(48) P. S. Skell and R. A. Plepys, manuscript in preparation.
(49) J. T. Keating, Ph.D. Thesis, The Pennsylvania State University, 1968.
(50) A. A. Humffray and L. F. G. Williams, *Chem. Commun.*, 616 (1965).

cathodic for the same interval. Free $RCO_2 \cdot$ generated during an anodic phase should be completely decomposed to $R \cdot$ and CO_2 in this time interval,[13] and Kolbe product R-R should be observed. The small yields of R-R eliminate free $RCO_2 \cdot$ as significant intermediates.

(5) Evidence is presented elsewhere[49] that dimer formation from alkyl radicals does not occur exclusively in the fluid medium, but to a considerable extent must occur on the platinum electrode, *i.e.*, adsorbed $R \cdot$.

(51) R. A. Plepys, Department of Chemistry, The Pennsylvania State University, unpublished results.
(52) Related to this is the fact that hydrocarbon formation does not occur immediately upon closing of the electrolysis circuit (DC); however, opening the circuit for a short time and then closing it causes immediate hydrocarbon evolution.[17] Dickinson and Wynne-Jones[17] ascribe this to the presence of adsorbed carboxylate radicals.

The 3,3-Dimethyl-2-butyl Cation. Pinacolyl Cation

Philip S. Skell and Paul H. Reichenbacher[1]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received December 22, 1967

Abstract: The 3,3-dimethyl-2-butyl (pinacolyl) cation is generated by anodic oxidation of potassium 2,3,3-trimethylbutanoate at a bright platinum electrode. At pH below 14, the cation reacts mainly by rearrangement to the tertiary cation; higher hydroxide ion concentrations are more effective in trapping the unrearranged cation.

The free 3,3-dimethyl-2-butyl (pinacolyl) cation was produced by the rearrangement of 3,3-dimethyl-1-butyl cation.[2] The direct generation of this cation by anodic oxidation of the pinacolyl radical is an alternate route to this elusive neopentyl-like cation.
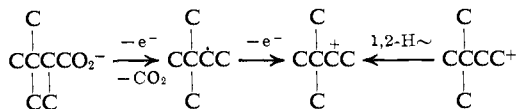
Results and Discussion

Potassium 2,3,3-trimethylbutanoate was electrolyzed at bright platinum electrodes; both carbonium ion and free-radical products were obtained (Table IV). The saturated hydrocarbon products, bipinacolyl and 2,2-dimethylbutane, are typical Kolbe electrolysis products derived from radicals with unrearranged skeletons. The bulk of the products, olefins, alcohols, and esters, are more oxidized than the radical by one electron and for the main have rearranged carbon skeletons. If the 2,2-dimethylbutane is half of a

radical disproportionation couple, an equivalent amount of 3,3-dimethyl-1-butene would be produced. Subtraction of this quantity of olefin and the saturated hydrocarbons leaves the carbonium ion products (Table I). The carbonium ion derived products are those suggested by the first modern theory in this field.[3]
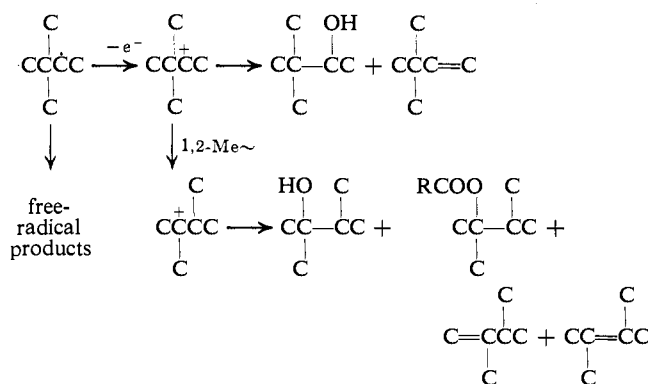
Two important aspects of this chemistry of the free pinacolyl cation are: (1) although it generally is con-

(1) From the Ph.D. Thesis of P. H. R., The Pennsylvania State University, 1967.
(2) P. S. Skell and P. H. Reichenbacher, *J. Am. Chem. Soc.*, **90**, 2309 (1968).
(3) F. C. Whitmore, *ibid.*, **54**, 3274 (1932).