

Society, for partial support of this work. We are also grateful to the National Science Foundation (GP-33909X) for partial support. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

References and Notes

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- For a prior application of this technique, see W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971).
- (a) Tris[[3-(heptafluoropropylhydroxymethylene)-d]camphorato]europium(III); H. L. Goering, J. N. Eikenberry, and G. S. Koerner, *J. Am. Chem. Soc.*, **93**, 5913 (1971). (b) The data of Table I are confirmed by the $^{13}\text{C}_7$ resonances of the pyrolyzed samples. At 40% enrichment, the natural abundance ^{13}C contributes only negligibly to the C_7 signal, which is then due entirely to the presence of the labeled species B and C. Because of the β deuterium in B, its C_7 resonance occurs slightly upfield (42.69 ppm) relative to that of C (42.79 ppm). Integration of the peak areas gives ratios of B/C = 3.8 ± 0.2 and 4.0 ± 0.2 for the two samples. These values compare well with those from Table I, 3.3 ± 0.5 and 4.4 ± 0.1 .
- A hypothetical mechanism for racemization would involve reversible [1,3] sigmatropy of C_8 from C_1 to C_3 through an achiral 5-methylenebicyclo[4.1.1]oct-2-ene intermediate. However, this process would leave the C_3 deuterium unscrambled and therefore would predict $k_3/k_{\alpha} = 0$. We find instead that $k_3 = k_{\alpha}$ within experimental error of $\sim 5\%$, so that this mechanism cannot be important.
- This (+) contaminant is not identical with D, since it has a C_3 deuterium rather than a C_1 deuterium. However, the polarimetric and ^{13}C analyses do not distinguish it from D itself.
- Kindly provided by Professor Martin Saunders and slightly modified by Dr. B. K. Carpenter for use on the PDP-1145 system.
- The labor of guessing trial rate constants is substantially reduced in the present case by assuming perfect kinetic symmetry for Scheme I (that is, no secondary isotope effect) and solving directly for the rate constants using an explicit solution for the general symmetrical four-component system kindly provided to us by Dr. Barry K. Carpenter, Cornell University.
- We are indebted to a referee for this point.
- For recent studies of related bisallylic systems, see (a) D. Hasselmann, *Tetrahedron Lett.*, 3465 (1972), and 3739 (1973); (b) J. J. Gajewski, L. K. Hoffman, and C. N. Shih, *J. Am. Chem. Soc.*, **96**, 3705 (1974); (c) J. Japenga, M. Kool, and G. W. Klumpp, *Tetrahedron Lett.*, 1029 (1975); (d) R. W. Holder and R. E. Voorhees, Abstracts of Papers, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 20–25, 1977, ORGN 80; (e) R. Bishop, W. Parker, and I. Watt, *Tetrahedron Lett.*, 4345 (1977).
- The temperature dependences of k_3 and k_9 between 309.4 and 352.0 °C give activation parameters $\Delta H^\ddagger = 46.8 \pm 1.7$ and 48.0 ± 1.7 kcal/mol; $\Delta S^\ddagger = -1.4 \pm 3.0$ and 0.6 ± 3.0 eu.
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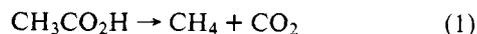
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Heterogeneous Photocatalytic Synthesis of Methane from Acetic Acid—New Kolbe Reaction Pathway

Sir:

Recent investigations have described the application of the principles of semiconductor electrodes (currently being studied in photoelectrochemical cells for the utilization of solar energy¹) to the design of systems for heterogeneous photocatalysis.^{2,3} In these systems the absorption of light on a semiconductor powder suspended in a liquid promotes electron-transfer reactions of substances in solution.⁴ Synthetic applications of these techniques have not yet been demonstrated. We report here the heterogeneous photocatalytic decomposition of acetic acid on n-type TiO_2 to yield (almost exclusively) methane and carbon dioxide:



This unprecedented facile and efficient decarboxylation of an unactivated (saturated aliphatic) carboxylic acid at ambient temperature to give the corresponding alkane contributes to

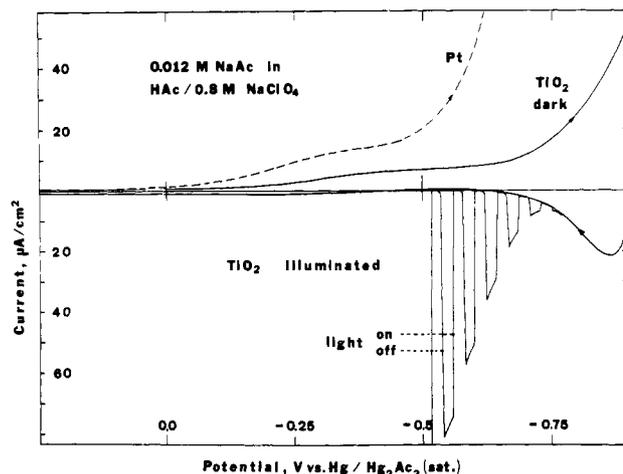


Figure 1. Current-potential curves for Pt and n-type TiO_2 (rutile, single crystal) in the dark and under chopped illumination with 450-W xenon lamp.

our understanding of photocatalysis at semiconductors⁵ and provides a new technique in synthetic organic methodology. Moreover it represents a third, and so far unknown, reaction pathway in the sequence of a Kolbe reaction.⁶

When a stirred, deaerated suspension of 100 mg of platinumized n-type TiO_2 powder⁷ in a mixture of 4.5 mL of glacial acetic acid and 45 mL of distilled water at 55 °C contained in a Pyrex cell was illuminated with white light from a 2500-W xenon lamp (operated at 1600 W), a continuous stream of gas bubbles was observed to rise out of the depth of the solution near the illuminated area. These gaseous products, which accumulated at a rate of 8.1 mL/h were collected in a gas volumetric system and analyzed by mass spectroscopy and gas chromatography. The mass spectrum (m/e (rel intensity)) consisted of signals of carbon dioxide, 44 (100); ethane,⁸ 30 (2), 29 (1.5), 28 (~ 7), 27 (2), 26 (1.5); methane,⁸ 16 (91), 15 (79), 14 (5); and hydrogen, 2 (4), with small background signals due to air (oxygen, 32 (2); nitrogen, 28 (~ 8)); and water, 18 (13). The ratio of methane to ethane of the gaseous products was estimated by gas chromatography to be 11:1. Moreover the yield of CO_2 was determined quantitatively⁹ in a subsequent run under identical conditions to account for 160 $\mu\text{mol/h}$ (corresponding to 3.7 mL of gas at 1 atm) and therefore for about half the volume of the gaseous reaction products, in full accord with eq 1. The dominant reaction products of the decomposition of acetic acid were carbon dioxide and methane (ratio $\sim 1:1$); only small amounts of ethane and hydrogen were formed (total ~ 10 vol %, in roughly a ratio of 1:1). Qualitatively and quantitatively similar results were obtained with pure acetic acid as solvent and reactant or with acetic acid containing 0.8 M sodium acetate. Side reactions attributable to photocatalytic decomposition of water seem to be unimportant. Blank experiments without TiO_2 photocatalyst (under 1 atm of O_2) and similarly with untreated TiO_2 powder (TiO_2 reagent, MCB, anatase, under N_2 atmosphere) under similar conditions as described above resulted in only minute amounts of CO_2 (trapped as BaCO_3) corresponding to $\sim 2 \mu\text{mol/h}$ ($\pm 1 \mu\text{mol/h}$ error limit).

The production of methane is surprising, in view of the usual products of a Kolbe reaction with acetic acid/acetate



and our recent results³ on the facile photoassisted decarboxylation of acetate of an illuminated n-type TiO_2 electrode in acetonitrile solution, giving almost exclusively carbon dioxide and ethane.

The photocatalytic activity of suspended TiO_2 powder can be correlated with the behavior of n-type TiO_2 electrodes in

photoelectrochemical measurements. As shown in Figure 1, the photoinduced oxidation of acetic acid (presumably as the acetate ion) on an illuminated n-type TiO₂ rutile single-crystal electrode takes place at more negative potentials than the reduction of acetic acid protons on the same material and even more negative than the reduction of platinum. Thus, the reduction of acetic acid on platinum and the photooxidation of acetate ion on n-type TiO₂ can easily take place simultaneously at the two electrodes under short circuit conditions, i.e., without applied potential. The curves also indicate that this occurs at a common potential of about -0.6 V vs. the Hg/Hg₂Ac₂ reference electrode¹⁰ and with an estimated quantum yield of ~3-5%. Thus the apparent ease of photocatalytic decomposition of acetic acid on platinized n-type TiO₂⁷ can be rationalized, since this powder can be thought to act as a multitude of small, short-circuited Pt-TiO₂ electrode systems, where the partial coverage with Pt essentially boosts the yield by lowering the otherwise significant overpotential of the hydrogen reduction.¹¹ Light of energy greater than band gap ($\geq \sim 3.0$ - 3.2 eV¹²) causes the formation of an electron-hole pair, whose recombination is partially prevented (presumably due to bending of bands caused by the equilibria $H^+ + e^- \rightleftharpoons H(\text{ads})$ or $2H^+ + 2e^- \rightleftharpoons H_2$ on the Pt). The low-lying holes thereby created lead to the oxidation of acetate, thus initiating the Kolbe process. The rapid decomposition of the CH₃CO₂· radical, leading to the CH₃· radical and CO₂, prevents any reverse reaction. Hypothetical at the moment are the further follow-up processes, but the observed formation of methane indicates that they are reductive. While the reduction potential of methyl radicals (in aqueous surroundings) is not known, it seems reasonable to assume the sequence reduction and protonation, especially in view of the fairly negative short circuit potential of the Pt-illuminated TiO₂ pair in the electrochemical measurements (~ -0.6 V). Such a sequence, at any rate, is in full accord with the following experiment with partially monodeuterated acetic acid produced by addition of 99.7% D₂O as cosolvent in the initially described experiment which theoretically produced a mixture CH₃CO₂D and CH₃CO₂H in the ratio 49:1 by exchange of the carboxylate protons.¹³ Irradiation of this solution with a suspension of platinized TiO₂ photocatalyst⁷ under inert atmosphere again led to gas evolution, with a slightly lower yield (5.5 mL/h), presumably as a consequence of the isotopic substitution. The mass spectral analysis revealed these gases to again consist of CO₂, CH₃CH₃ (undeuterated), methane (73% CH₃D, 27% CH₄), and hydrogen (H₂:HD:D₂ = 2:1:masked by He). This isotopic labeling pattern eliminates a mechanism involving hydrogen abstraction from the acetic acid methyl and supports the postulated origin of one of the methane hydrogens to be an acidic solution proton or deuteron.

Apparently the TiO₂ powder acts in a dual function causing the photooxidation of acetate and the reduction of intermediately formed methyl radicals, a property not found at metal electrodes under the usual Kolbe conditions where the electrode potential is maintained at a very positive value. Several unique properties of these partially metallized large-band-gap semiconductor powder photocatalysts emerge: (1) they are potentially strong photooxidizing agents, since the quasi-Fermi level of holes under irradiation lies near the valence band edge at very positive potentials;¹⁴ (2) their large surface area¹⁵ allows a low (surface) concentration of radical intermediates, thus suppressing radical-radical reactions (dimerization, disproportionation); (3) under proper conditions the intermediates are formed near reducing sites, since the quasi-Fermi level of electrons lies near the conduction band.¹⁴ These properties allow this heterogeneous photocatalytic Kolbe reaction to branch off from the normal paths (to ethane or methanol) with channeling of the intermediate methyl radicals into a reductive route to methane. The possible extension of

this reaction to other synthetically as well as mechanistically more interesting aliphatic or alicyclic carboxylic acids will hopefully clarify the mechanistic and synthetic scope of this alternate photo-Kolbe reaction. The effect of changes in experimental variables, the flux of light, and the dark rest potential of the semiconductor on the distribution of reaction products will also be subjects of upcoming investigations in this laboratory.¹⁶

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- (5) Reaction 1 actually is exoenergetic with a standard free-energy change $\Delta G_f^\circ = -12.5$ kcal/mol (data taken from "Handbook of Chemistry and Physics", 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p D-61).
- (6) See, e.g., J. H. P. Utley in "Technique of Electroorganic Synthesis", Vol. 1, N. L. Weissenberger, Ed., Wiley-Interscience, New York, N.Y., 1974, p. 793; L. Ebersohn in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973.
- (7) Produced by illuminating for 4 h a deoxygenated suspension of 100 mg (white) of n-type TiO₂ powder (anatase grade, MCB, particle size 125-250 μm) in 20 mL of platinizing solution (H₂PtCl₆ in dilute HCl, corresponding to ~ 100 mg of Pt) with the white light of a 2500-W xenon lamp, operating at 1600 W, followed by neutralization of the acidic solution, addition of 100 mg of hydroquinone, and 12-h reaction of 50 °C under nitrogen. The now grayish powder was extensively washed with distilled water and dried for 1 h at 120 °C. The distribution of platinum on the TiO₂ particle surface was found by electron microscopy to be uniform down to a resolution of $< 1 \mu\text{m}$.
- (8) Reference data for mass spectra (m/e (rel intensity)) (from "Selected Mass Spectral Data", American Petroleum Institute, 1972) of ethane, 30 (26), 29 (21), 28 (100), 27 (33), 26 (26); and methane, 16 (100), 15 (85), 14 (6).
- (9) The evolving gases were swept out of the reaction chamber by a slow stream of nitrogen and were led through a 1 N NaOH solution saturated with Ba(OH)₂; the precipitate, BaCO₃, was determined gravimetrically.
- (10) The reference electrode, Hg/mercurous acetate in acetic acid/0.05 M sodium acetate and 0.7 M sodium perchlorate, has a potential of roughly 0.45 V positive of an aqueous SCE.
- (11) Similarly the overpotential for reduction of water on a SrTiO₃ single-crystal electrode was found to be lowered by Pt coating; M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, *J. Solid State Chem.*, **22**, 17 (1977).
- (12) The band gap for the anatase form of TiO₂ was reported to be slightly larger than for rutile, 3.23 and 3.02 eV, respectively; V. N. Pak and N. G. Ventov, *Russ. J. Phys. Chem.*, **49**, 1489 (1975).
- (13) A routine mass spectrum of the reaction mixture after the experiment gave the much lower ratio CH₃CO₂D:CH₃CO₂H of ~ 3 :1 (presumably because of exchange in the mass spectrometer), but clearly established on upper limit of $\leq 4\%$ monodeuteration of the acetic acid methyl group.
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- (15) The active surface area of the powder can be estimated from the particle size (diameter $\sim 150 \mu\text{m}$) and grain size ($\sim 0.2 \mu\text{m}$) to be 10^4 to $2 \times 10^5 \text{ mm}^2$.
- (16) The support of this research by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung (to B.K.) and by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

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Helium(I) Photoelectron Spectrum of Tropyli Radical

Sir:

There has been much recent discussion¹ of the structures and stabilities of C₇H₇ cations. We wish to report the initial results of our investigation of the photoelectron spectrum (pe) of tropyli radical which bear on the stability (heat of formation) of the tropylium ion and the structure of the tropyli radical. The spectrum (Figure 1, top) was obtained by flash vacuum pyrolysis² of bitropyl (Figure 1, bottom) in a manner similar to