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OXIDATIVE ANODIC TOSYLAMIDATION AT A VANADIUM ELECTRODE

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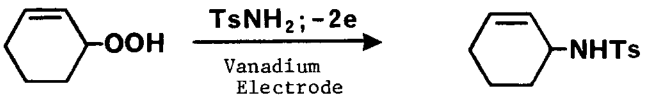
Cyclohexene hydroperoxide is converted efficiently to cyclohexenyl tosylamide by electrolysis only at a vanadium anode.

Since electrochemical reactions occur at electrode surfaces, one might hope for specific chemistry characteristic of the electrode material, not just of the potential. Examples are known for electrochemical hydrogenations, in which an acetylene is reduced at a nickel cathode but not at mercury.[1] We now wish to describe a curious anodic substitution reaction which occurs readily with a vanadium electrode but not with more common materials as anodes.

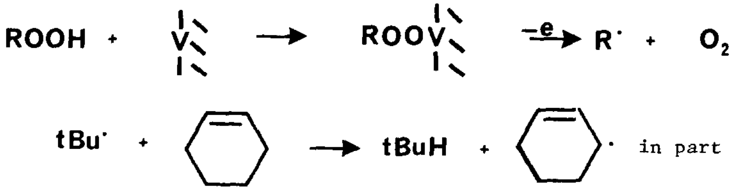
The process examined was the electrochemical oxidation of cyclohexene in carefully purified acetonitrile with toluenesulfonyl amide[2] and 0.1 N tetrabutylammonium fluoborate as supporting electrolyte. All reactions were performed in a double H cell (i.e. the anode and cathode compartment separated by two fritted discs and a central compartment). The 8 ml working compartment contained the anode and a Ag/AgCl reference electrode, while the cathodic compartment contained a Pt electrode. Background current was typically ∿3 mA with a cutoff of +2.0 V.

When 50 μl of distilled cyclohexene was electrolyzed with 100 mg tosylamide at a vanadium rod anode a large irreversible wave appeared at +1.6 V. Preparative electrolysis at +1.8 V showed that only 20% of the initially added "cyclohexene" was oxidized, but it was quantitatively converted to 1-tosylamido-2-cyclohexene.[3] It was easily established that the substrate for this reaction is in fact cyclohexenyl hydroperoxide, present in the distilled cyclohexene. The authentic hydroperoxide[4] is quantitatively converted to the tosylamide on passage of 2 Faradays/mole, and the yield is unaffected by added pure cyclohexene.



The remarkable observation is that this process is apparently unique to vanadium. Thus when a platinum electrode is used instead a low current quickly dies off and the tosylamide product is not formed. This is also true if the system is pre-electrolyzed without the cyclohexenyl hydroperoxide with a vanadium electrode; substitution of a platinum electrode and addition of the hydroperoxide leads to no product, showing that whatever soluble vanadium species might be produced on electrolysis cannot substitute for the vanadium electrode itself. Osmium, manganese, or chromium electrodes were rapidly destroyed or coated, but led to none of the allylic tosylamide. Aluminum was stable, but also led to no product. Only a carbon electrode was able to pass a low current and produce a trace of cyclohexenyl tosylamide, but the vanadium electrode was far superior.

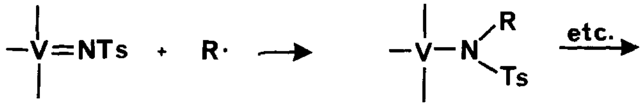
A mixture of pure cyclohexene and t-butylhydroperoxide was oxidized at vanadium to 60% t-butyl tosylamide[5] and 30% cyclohexenyl tosylamide. Di-t-butylperoxide underwent no reaction. Thus the vanadium electrode is performing two special functions. First of all, it is oxidizing the hydroperoxide group, possible by specific coordination by analogy with the solution chemistry of hydroperoxides and vanadyl compounds.



in part

Then the product radical must lose another electron and be trapped by tosylamide (in either order). Since it is hard to imagine that either a radical or a cation would be efficiently captured by tosylamide in free acetonitrile solution, we suggest that this trapping occurs at the electrode by a species analogous to a vanadyl group.

e.g.



Of course the detailed mechanisms involved in these reactions are not yet clear, nor are the reasons for the special effect of vanadium established. However, this work does demonstrate the tosylamide can be incorporated efficiently in anodic processes, as an approach to oxidative amination. Perhaps more important, our observations suggest that other anodic processes might also show specific effects related to the inorganic chemistry of the electrode material.[6]

1. K. N. Campbell and E. E. Young, J. Amer. Chem. Soc., 65, 965 (1943).
2. Chemical amidations in which tosylamide can be considered a substitute for the water involved (intellectually) in oxygenations have been described by Sharpless. Cf. K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, J. Amer. Chem. Soc., 97 2305 (1975).
3. K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, J. Amer. Chem. Soc., 98 269 (1976).
4. Prepared by the procedure in Chem. Abstr., 57, 14966h (1962).
5. V. I. Markov and S. I. Burmistrov, Zh. obschei Khim., 35, 153 (1965).
6. Support of this work by the National Science Foundation, and an NSF Predoctoral Fellowship to R. Q. Kluttz, are gratefully acknowledged.

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