Notes

Inhibitors in the Palladium-Catalyzed Hydrogenation of Aryl Nitro Groups

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In liquid-phase hydrogenations of aromatic nitro compounds to aromatic amines, the slurry catalyst of choice usually is powdered palladium on carbon. This is so both for preparative laboratory organic syntheses and for industrial processes, such as the hydrogenation of dinitrotoluene to toluenediamine. Thus, the inhibitory effects of possible impurities in such reductions are of practical importance as well as of academic interest.

There is very little literature on the inhibition of palladium-catalyzed hydrogenations of nitro groups. Extrapolation of results from the many excellent published studies of poisoning is difficult since inhibitory effects depend on the nature of the substrate being hydrogenated. For example, sodium hydroxide and sodium methoxide do not inhibit the reduction of nitrobenzene to aniline under conditions where reduction of a less strongly adsorbed substrate, such as an olefin, is severely inhibited.[1]

A number of inorganic anions, inorganic cations, and organic compounds were tested as inhibitors in the palladium-catalyzed hydrogenation of *p*-nitrotoluene to *p*-toluidine. The study was made under mild conditions of temperature and pressure, and the potential inhibitors were at a level of about 5 mole % based on *p*-nitrotoluene, much higher than trace contamination. Thus, lack of inhibition indicates that the contaminant is quite innocuous, and slight inhibition suggests that the contaminant might not be troublesome at a lower concentration and/or under more severe reaction conditions.

No inhibition was shown by sodium nitrate, acetate, sulfate, carbonate, phosphate, hydroxide, fluoride, bromide, and chloride. Increasing the amount of sodium chloride to 15.4 mole % based on *p*-nitrotoluene did not change the reaction rate. Inhibition was caused by both sodium and potassium nitrites, with an approximately threefold increase in reaction time. This is of interest because of possible contamination with nitrite ions in some products from nitrosation and nitration reactions. Sodium sulfite caused complete poisoning after about one-third of the reaction had been slowly completed. Complete poisoning was produced by sodium iodide, cyanide, sulfide, and bisulfite. Decreasing the amount of sodium iodide to 2.56 mole % based on *p*-nitrotoluene still resulted in complete poisoning.

No inhibition was shown by ferrous chloride. The reaction time was increased about 1.5-fold by nickel(II) nitrate, and about twofold by ferric chloride, ferric nitrate, cobalt(II) nitrate, and chromium(III) nitrate. More severe inhibition was caused by zinc nitrate, with an approximately tenfold increase in half-life. Complete poisoning was produced by copper(I) chloride, copper(II) chloride, copper(II) nitrate, silver nitrate, aluminum nitrate, and lead nitrate. Poisoning by copper compounds is of practical importance because their use in many preparative reactions sometimes results in the contamination of aromatic nitro compounds. For example, copper compounds are used in the replacement of the halogen of aryl halides by nucleophilic reagents as aqueous alkali, ammonia, amines, and cyanides; in replacement of the diazonium group of aryl diazonium salts by a variety of reagents; and in the synthesis of diaryls by condensation of aryl halides or diazonium salts.

No inhibition was caused by *n*-octyl chloride, chlorobenzene, bromobenzene, aniline, piperidine, sodium methoxide, phenol and *p*-nitrophenol, using 5.13 mole % based on *p*-nitrotoluene. Nitrophenols have been reported to be severe poisons in the palladium-catalyzed hydrogenation of dinitrotoluenes in the absence of solvents or diluents.[2] There was no indication of such behavior under our experimental conditions.

The reaction time was increased about twofold by *p*-nitroso-N-methylaniline and about sixfold by *p*-nitrosodiphenylamine. The addition of N-nitrosodiphenylamine produced an induction period of about one hour followed by hydrogenation at about one-third the rate of the uninhibited reaction. The inhibition caused by both C-nitroso- and N-nitrosoarylamines is noteworthy because of the presence of nitroso groups in certain aromatic nitro compounds, either as part of the nitro compound or a contaminant.

The effect of phenyl disulfide was investigated at very low concentrations. No inhibition was caused by 0.0026 mole % based on *p*-nitrotoluene, and an approximately fivefold increase in reaction time was produced by 0.0051 mole % based on *p*-nitrotoluene. Thus, phenyl disulfide produces considerable inhibition at a level of about 50 moles of inhibitor per million moles of nitro compound.

Experimental

Each experiment was run in a Paar shaker type pressure reaction apparatus (Paar Instrument Co., series 3910) at room temperature and a hydrogen pressure of about 4 atm.

A 50-ml. charge was used, containing 2.68 g. (19.5 mmoles) of *p*-nitrotoluene in a mixture of 2-propanol and water (4:1 volume ratio) and 0.05 g. of a 5% palladium-on-carbon catalyst containing 50% water, *i.e.*, 0.025 g. of 5% palladium on carbon (Engelhard Industries, Inc.). The concentration of *p*-nitrotoluene was 53.5 g./l. or 0.39 mole/l. The concentration of 5% palladium on carbon was 0.5 g./l., 0.93 wt. % based on *p*-nitrotoluene, or 1.3 g./mole *p*-nitrotoluene. One millimole of the compound to be tested as an inhibitor (0.02 mole/l., 5.13 mole % based on *p*-nitrotoluene) usually was added. Reagent-grade chemicals were used throughout.

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(1) R. Baltzly, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

(2) L. D. Winstrom and R. D. Samdahl, U. S. Patent 2,976,320 (March 21, 1961); British Patent 832,153 (April 6, 1960).

For the most part, reaction rates were compared on the basis of half-life, the time required for completion of approximately one-half of the reaction as determined by hydrogen absorption. The total gas absorption was about 5 p.s.i., and the half-life for an uninhibited reduction of *p*-nitrotoluene to *p*-toluidine was about 9 ± 1 min., with the rate roughly zero order with respect to *p*-nitrotoluene. Since there was no attempt to control temperature, the results are semiquantitative. Nevertheless, gross differences in rate were reproducible and meaningful.

Controlled Potential Electrolytic Oxidation of Anthracene in Acetonitrile[1]

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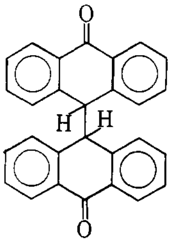
Controlled potential electrolysis has been established as a useful technique in synthetic organic chemistry, especially when the desired product is itself easily oxidized or reduced.[2a,b,3] The efficacy of this approach to synthesis problems is well illustrated by the work of Lingane, Swain, and Fields who successfully reduced 9-(*o*-iodophenyl)acridine to the dihydro derivative.[4] Theory and techniques of controlled potential electrolysis have been adequately discussed by Lingane.[5] Most controlled potential electrolytic syntheses have utilized direct electrolysis of the starting material at the working electrode to produce the desired product, although so-called substitution techniques also have been used.[1,2]

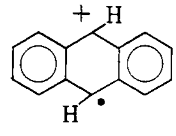
Recent voltammetric studies of aromatic hydrocarbons is acetonitrile solution have suggested that the anodic waves of these compounds are due to the removal of π-electrons. The ion radicals formed are very reactive species and in the case of naphthalene polymerize rapidly to coat the anode and cause a rapid decrease of the electrolysis current.[6] Lund also showed that pyridine in an electrolysis solution of anthracene in acetonitrile reacted with the 9,10-dihydroanthracinum radical ion to form the dipyridinium salt. The present work was undertaken in an attempt to extend the technique to the use of other nucleophiles which might produce useful derivatives of anthracene. Ethanol was selected with the expectation that the 9,10-diethyl ether derivative of anthracene would be obtained. The electrolytic addition of ethoxy groups to furan using the constant current technique has been reported.[7]

Electrolysis of a saturated acetonitrile solution of anthracene which contained supporting electrolyte and was 0.45 *M* in absolute ethanol produced a white compound which was partially soluble (the remainder was recovered by adding water). The electrolysis product was shown to be bianthrone (I) (10,10′-bianthronyl).

Based on the observed formation of the dipyridinium perchlorate salt and on the amount of electricity consumed, Lund stated that the electrolytic oxidation of anthracene resulted in the loss of two π-electrons.[6] The production of bianthrone, however, would indicate that the anode reaction occurring in the present system involved the loss of only one π-electron from each anthracene molecule to form the free radical ion species (II) which then dimerized. The additional oxidation of any 9,9′-bianthryl formed was in fact predicted by Lund.[6]

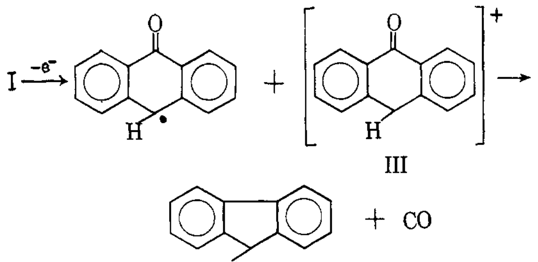


I



II

The following considerations would account for the observed peaks in the mass spectra and for the failure to observe a peak at *m/e* 386. Cleavage of the labile 10–10′ bond in bianthrone would likely occur upon electron impact and could produce the benzylically stabilized 10-anthrone radical and the highly stable aromatic fragment (III) with *m/e* 193. The peak at *m/e* 165 would appear upon loss of CO (twenty-eight mass units) from III in a manner analogous to that reported for anthraquinone.[8]



Experimental

Reagents and Solutions.—Eastman (Practical) acetonitrile was distilled from phosphorus pentoxide and used to prepare all solutions. Chemically pure sodium perchlorate (Amend Drug and Chemical Co.), dried at 150° for 24 hr. and stored over phosphorus pentoxide in a vacuum desiccator, was used to prepare the supporting electrolyte. Anyhydrous silver perchlorate was used on special order from Fisher Scientific Co. Other chemicals were reagent grade quality.

Apparatus.—A Sargent Model XV polarograph was used to record current–voltage curves. A modified[9] Kelley, Jones, and Fisher controlled potential coulometric titrator[10] was used as a potentiostat for all electrolyses and also to determine the exact working electrode potentials for the electrolyses as described later. Ultraviolet absorption spectra were recorded on a Beckman Model DK-2 spectrophotometer, infrared spectra on a Baird-Atomic Model KM-1 spectrophotometer, and mass spectra on a Bendix Time of Flight and on a Consolidated Model 21-103C mass spectrometer.

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[1] Abstracted from the thesis submitted by K. E. Friend for the M.S. degree in chemistry, University of Rhode Island, July, 1962.

[2] (a) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Co., New York, N. Y., 1958; (b) A. P. Tomilov, *Usp. Khim.*, 1462 (1961); *Russ. Chem. Rev.*, 639 (1961).

[3] F. D. Popp, H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962).

[4] J. J. Lingane, C. G. Swain, and M. Fields, *J. Am. Chem. Soc.*, **65**, 1348 (1943).

[5] J. J. Lingane, "Electroanalytical Chemistry," 2nd Ed., Interscience Publishing Co., New York, N. Y., 1958.

[6] H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

[7] N. Clauson-Kaas, *ibid.*, **6**, 569 (1952).

[8] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Van Nostrand Publishing Co., Princeton, N. J., 1960, pp. 271, 272.

[9] W. J. Curren, M.S. thesis, University of Rhode Island, 1960.

[10] M. T. Kelley, H. C. Jones, and D. J. Fisher, *Anal. Chem.*, **31**, 488 (1959).