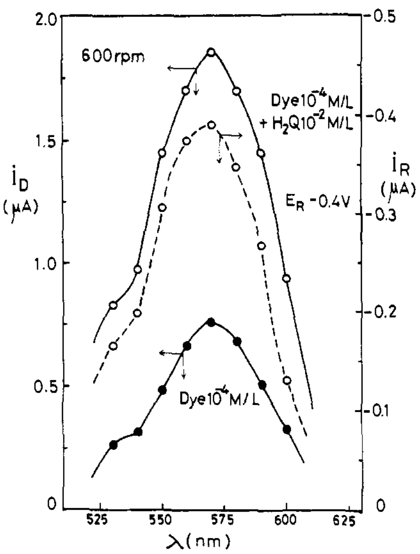

Figure 2. Currents observed at the CdS disk and Au ring electrodes during spectral sensitization with rhodamine B and supersensitization with hydroquinone: i_D, disk current; i_R, ring current; —●—, disk current with 10^{-4} *M* of rhodamine B; ○ (solid line), disk current with 10^{-4} *M* of rhodamine B + 10^{-2} *M* of hydroquinone; ○ (dashed line), ring current with 10^{-4} *M* of rhodamine B + 10^{-2} *M* of hydroquinone.

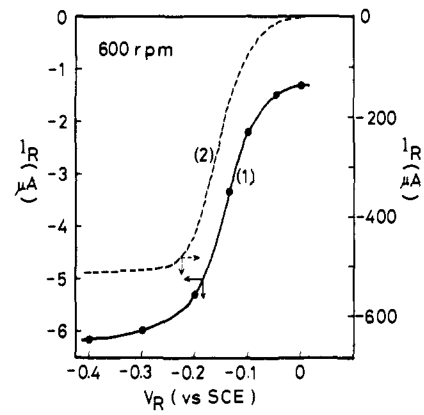

Figure 3. Current-potential characteristics for (1) the ring electrode under supersensitization on CdS disk (10^{-4} *M* of rhodamine B + 10^{-2} *M* of hydroquinone) and (2) the Au ring electrode (10^{-3} *M* of quinone).

the ring electrode where the supersensitization reaction occurred on the CdS disk electrode was compared with that of the Au ring electrode where only quinone was present in the solution. The two current-potential curves coincide fairly well, as depicted in Figure 3. From these observations we conclude that hydroquinone is oxidized to quinone in the course of supersensitization.

We measured the collection efficiency ($-i_R/i_D$) for the CdS disk-Au ring system as a function of the rotation rate in the range 200–1000 rpm. Both disk photocurrent under the illumination with the constant intensity and ring reduction current were steady state quantities and independent on the rotation rate. Therefore, no appreciable change of the collection efficiency was observed. According to the theory of the RRDE system,[6] the collection efficiency for this rotation rate region is expected to decrease as the rotation rate increases, provided that the rate of the first-order reaction between hydroquinone and the supposed oxidized species of rhodamine B is the range of 10^{-2} to 2×10^2 sec^{-1}. The present result indicates that the reaction rate is much greater than 10^2 sec^{-1}.

When 1,1′-diethyl-2,2′-quinocyanine was used as the sensitizing dye, just as in the case of rhodamine B, the reduction of quinone was detected at the Au ring electrode. Furthermore, when potassium ferrocyanide was added to the dye-containing electrolyte solution, reduction of ferricyanide ion was detected at the ring electrode.

Based upon the results of the present study, we conclude that reducing agents undergo oxidation in the course of photoelectrochemical supersensitization at the CdS single-crystal electrode.

References and Notes

(1) H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **72,** 437 (1968).
(2) K. Hauffe, H. J. Danzmann, H. Pusch, J. Range, and H. Volz, *J. Electrochem. Soc.*, **117,** 993 (1970).
(3) A. Fujishima, E. Hayashitani, and K. Honda, *Seisan Kenkyu,* **23,** 31 (1971).
(4) A. Fujishima, E. Hayashitani, and K. Honda, *Seisan Kenkyu,* **23,** 363 (1971).
(5) A. Fujishima, T. Watanabe, O. Tatsuoki, and K. Honda, *Chem. Lett.*, 13 (1975).
(6) W. J. Albery and S. Bruckenstein, *Trans. Faraday Soc.*, **62,** 1946 (1966).

Akira Fujishima,* Takashi Iwase
Faculty of Technology, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama, Japan

Tadashi Watanabe, Kenichi Honda
Institute of Industrial Science, University of Tokyo
Roppongi, Minato-ku, Tokyo, Japan

Received January 28, 1975

Formation of Ruthenium(II) Nitrile Complexes by Reaction of Hexaammineruthenium(III) with Aldehydes

Sir:

Recent reports have shown that under alkaline conditions coordinated ligands may effect nucleophilic attack at carbonyl centers in organic compounds.[1-4] For example, reactions of Co(III) and Pt(IV) ammines with ketones yield the corresponding Co(III) and Pt(IV) imine complexes.[5a] A similar reaction between hexaammineruthenium(III) and diones produces the corresponding Ru(II) diimine.[5a]

We now wish to report the formation of nitrilepentaammineruthenium(II) complexes, $(H_2N)_5Ru{\cdot}NCR^{2+}$ (R = $-CH_3$ or $-C_6H_5$), in the reaction of hexaammineruthenium(III), $Ru(NH_3)_6{}^{3+}$, with the appropriate aldehydes. This appears to be the first report of the formation of a nitrile from the reaction of an aldehyde with a transition metal ammine nucleophile.[5b]

A pK_a of approximately 12.4 has been reported[6] for the $Ru(NH_3)_6{}^{3+}$ ion, suggesting almost complete deprotonation in 1 *M* OH^-. Solutions of approximately 0.03 *M* $[Ru(NH_3)_6]Br_3$ containing a 100-fold excess of acetaldehyde or benzaldehyde react rapidly (complete in less than 1 min based on color change) to produce the nitrile complexes; addition of aqueous $NaClO_4$ precipitates the solid products. The isolated solids show infrared bands in the 2200-cm^{-1} ($\nu_{C\equiv N}$) region of the spectrum as well as bands characteristic of Ru(II) ammines in the 1300-cm^{-1} region.[7] The ultraviolet-visible and infrared spectra of the products are in good agreement with those reported in the literature[8] for the pentaammineruthenium(II) complexes of benzo- and acetonitrile prepared by the direct action of the respective nitriles on $Ru(NH_3)_5H_2O^{2+}$.

The overall reaction may be represented by the equation

$$(H_3N)_5Ru^{III}NH_3{}^{3+} + 2OH^- + RCHO + X \rightarrow (H_3N)_5Ru^{II}NCR^{2+} + 3H_2O + X^-$$

where X represents unidentified *oxidant*. The driving force of this reaction is probably stabilization of the ruthenium(II) nitrile species due to ability of the Ru(II) to back-bond to unsaturated nitrogen ligands;[9,10] a similar explanation has been involved to explain formation of the Ru(II) diimine species.[5] It is of interest, however, that the diimine case requires the participation of an unidentified *reductant* to obtain an overall balanced equation.[11]

The possibility that the reaction goes through the ruthenium(III) nitrile intermediate seems unlikely because ruthenium(III) nitriles are rapidly hydrolyzed by base to amide complexes.[12]

Investigations are continuing to establish the nature of the oxidant(s), elucidate the kinetics, and explore synthetic usefulness of this reaction.

References and Notes

(1) B. T. Golding, J. MacB. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 3003 (1974).

(2) J. D. Bell, A. R. Gainsford, B. T. Golding, A. J. Herlt, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 980 (1974).

(3) D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, **95**, 7281 (1973).

(4) J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 2634 (1974).

(5) (a) I. P. Evans, G. W. Everett, Jr., and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 139 (1975). (b) We have recently discovered a report (W. Brackman and P. J. Smit, *Recl. Trav. Chim. Pays-Bas*, **82**, 757 (1963)) describing the synthesis of aromatic and aliphatic nitriles in methanol solutions containing $CuCl_2 \cdot 2H_2O$, ammonia, $NaOCH_3$, and a variety of aldehydes (or alcohols oxidizable to aldehydes in these solutions). Nitrile yields of 10–90% were obtained after 6 hr at 30° in oxygen-saturated solutions (and much smaller yields with cupric as oxidant).

(6) D. Wayshort and G. Navon, *Chem. Commun.*, 1410 (1971). This value may be erroneous, see J. N. Amer. *J. Inorg. Nucl. Chem.*, **35**, 2067 (1973). Our observation that the reaction is much slower in 0.01 *M* than in 1 *M* NaOH is consistent with a path involving the amidopentaammine as the reactive species.

(7) Ruthenium ammine complexes can be readily distinguished as containing di- or trivalent ruthenium on the basis of their ir NH_3 bands in the 1200–1400-cm^{-1} region. A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

(8) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

(9) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(10) P. C. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

(11) A possibly related reaction is the oxidation of $Ru(en)_3^{2+}$ to the diimine, $en_2Ru(NH{=}CHCH{=}NH)$ by molecular oxygen reported by D. F. Mahoney and J. K. Beattie, *Inorg. Chem.*, **12**, 2561 (1973).

(12) A. W. Zanella and P. C. Ford, *Inorg. Chem.*, **14**, 42 (1975) report a second-order rate constant for the hydrolysis of $(H_3N)_5Ru^{III}NCCH_3^{3+}$ of 220 sec^{-1}; in 1 *M* OH^-, this corresponds to a half-life of about 0.003 sec. For $(H_3N)_5Ru^{III}NCC_6H_5^{3+}$ the rate constant in 1 *M* OH^- is 2000 sec^{-1} and the corresponding half-life about 0.0003 sec.

Kenneth Schug,* Charles P. Guengerich
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616

Received April 22, 1975

Photoelectron Spectrum and Gas-Phase Basicity of Manxine. Evidence for a Planar Bridgehead Nitrogen

Sir:

The bicyclic amine manxine, **1**, has recently been prepared by Leonard and coworkers.[1] Space-filling (CPK) molecular models of this amine show that it is highly strained as a result of transannular interactions between the hydrogens in the three three-membered bridges. The crystal structure of the hydrochloride salt of manxine indicates that these bridges flatten by expanding the C-C-C angles in the three-membered bridge to 117–120°, while the bridgehead C-C-C and C-N-C angles are 114–116°.[2,3] Molecular models of manxine suggest that much of the transannular strain can be relieved by permitting the nitrogen to assume a planar geometry. Recent force field calculations and the high solvolytic reactivity of manxyl chloride have placed the strain relief for conversion of manxyl chloride (bridgehead C-C-C $\angle \simeq$ 115°) to a planar manxyl cation at ca. 6–8 kcal/mol.[4] Since the inversion barriers of alkylamines are only ca. 4–6 kcal/mol,[5] it is expected that there should be more than sufficient strain energy relief to overcome the nitrogen inversion barrier for manxine to adopt a planar bridgehead configuration. We report here the gas-phase photoelectron spectrum and gas-phase basicity of manxine, which provide evidence for a planar configuration at nitrogen in manxine.

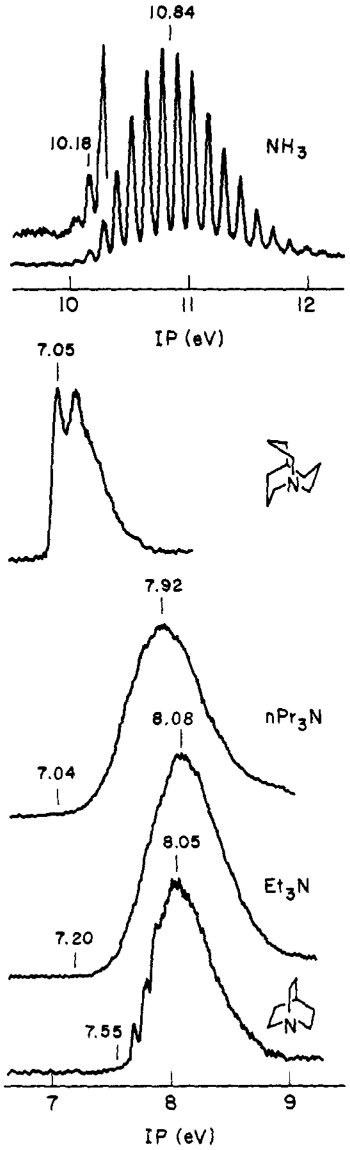

Figure 1. Photoelectron spectra for the first (lone pair) bands in manxine and related amines at 25°. The energy scale for NH_3 has been offset to show its peak shape relative to the alkylamines.

The photoelectron spectrum of ammonia (Figure 1) shows vibrational structure with a frequency (ca. 970^{-1}) characteristic of the nitrogen inversion.[6] The radical cation produced is expected to have a planar equilibrium geometry.[6a] From magnified scans near the onset of the first band in the ammonia spectrum, weak bands appear at 10.07 and at 10.18 eV.[7] Although alkyl substitution generally shifts the position of the nitrogen lone pair band strongly and broadens and obscures the vibrational fine structure, the shapes and widths of the bands stay remarkably similar to the envelope of the ammonia peaks with the difference between the onset (adiabatic IP) and the vertical IP usually 18–21 kcal/mol.[7,8] This is illustrated for triethyl- and tri-*n*-propylamine in Figure 1 and Table I.