

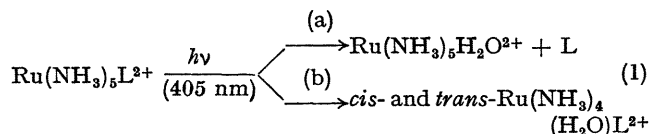
Quantum Yields for the Photoaquation Reactions of $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ and Related Complexes: An Unusual Dependence on Acid Concentration

By PETER C. FORD,* DONALD A. CHAISSON, and DANIEL H. STUERMER

(Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California, 93106)

Summary The quantum yield for pyridine displacement by aquation from $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ on irradiation at the metal-to-ligand charge-transfer band is a function of the solution pH indicating competitive acid-dependent and acid-independent reactions of a short-lived intermediate or excited state.

PREVIOUSLY we have shown¹ that photolysis at the metal-to-ligand charge transfer (MLCT) band (408 nm) of the penta-amminepyridineruthenium(II) cation leads to several photoaquation products [equation (1), L = pyridine]. We report here that the specific quantum yield (Φ_{1a}) for the photoaquation of pyridine from $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ [equation (1a)] is a complicated function of the acid concentration of the photolysis solution. To our knowledge, this is



the first report of a direct relationship between solution pH and the photoaquation quantum yield for a metal ammine complex which does not display ground-state equilibrium protonation or deprotonation reactions under the photolysis conditions.

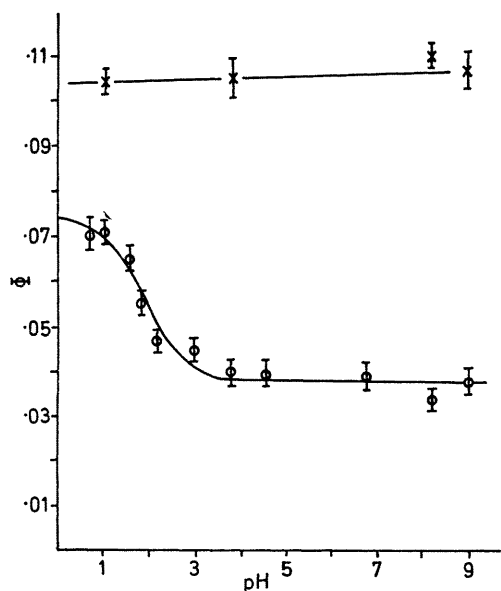


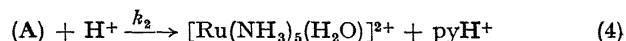
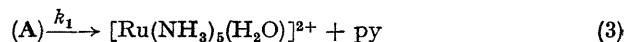
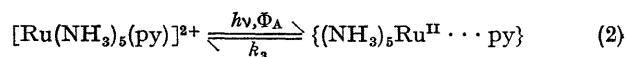
FIGURE. Plot of Φ_L (initial) vs. pH for photolyses of $[\text{Ru}(\text{NH}_3)_5(\text{benzotrile})][\text{BF}_4]_2$ [\times , $(5 \pm 3) \times 10^{-5}$ M] and of $[\text{Ru}(\text{NH}_3)_5(\text{pyridine})][\text{BF}_4]_2$ [\circ , $(5 \pm 1) \times 10^{-5}$ M].

Conditions: $25 \pm 1^\circ$, $\mu = 0.2$ M, buffers; pH 0.72–3.00, NaCl–HCl; pH 3.80, potassium acid phthalate; pH 4.6, acetate–acetic acid; pH 6.73, HPO_4^{2-} – H_2PO_4^- ; pH 8.22, tris(hydroxymethyl)methylamine; pH 8.95, NH_3 – NH_4^+ . Lower solid line is a theoretical curve based on equation (5).

The products of reaction (1b), *cis*- and *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{py})]^{2+}$, display MLCT bands of intensity and λ_{max} very similar to those of the starting material while $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$, the product of reaction (1a), is essentially transparent in the visible region.² By monitoring the decrease in the 408 nm band intensity, the quantum yield (Φ_{py}) for pyridine loss from the Ru(II) co-ordination sphere may be determined. Quantum yield and product studies are complicated by photolyses of products having co-ordinated pyridine, so Φ_{1a} is determined by extrapolating a plot of Φ_{py} versus photolysis time (t) to the $t = 0$ intercept.

The lower curve in the Figure illustrates the effect of solution pH on Φ_{1a} (L = pyridine). We have observed similar pH sensitivity of Φ_{py} (initial) for the $\text{Ru}(\text{NH}_3)_5^{2+}$ complex of 4-picoline (λ_{max} 398 nm, 405 nm irradiation). However, Φ_L (initial) for MLCT photolysis of the benzonitrile complex, $[\text{Ru}(\text{NH}_3)_5(\text{C}_6\text{H}_5\text{CN})]^{2+}$ (λ_{max} 376 nm,³ 366 nm irradiation) is essentially pH-independent (Figure).

The pH effect on Φ_{1a} for the pyridine complexes may indicate an excited state or subsequent intermediate which can competitively return to starting material or go to products by acid-independent and acid-dependent pathways to give the kinetic scheme illustrated [equations (2)–(4)]. A possible such species is a short lived, solvent caged Ru(II)–pyridine pair (A) in which the co-ordinate bond is broken or very substantially weakened. This intermediate could thermally reunite to give $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ or diffuse apart to give aquation products [equations (2) and (3)]. The $[\text{H}^+]$ sensitivity might be the result of competitive protonation of the pyridine in (A) followed by diffusion of the



pyridinium ion away from the Ru(II) (equation 4). If Φ_A is the acid independent quantum yield for the photolytic formation of (A), this mechanism predicts that the observed quantum yield Φ_{1a} will be a function of $[\text{H}^+]$ [equation (5)]. With $\Phi_A = 0.074$ moles/einstein, $k_2 = (138 \text{ M}^{-1})k_1$, and $k_3 = 0.95k_1$, the curve generated by equation (5) predicts

$$\Phi_{1a} = \Phi_A \left(\frac{k_1 + k_2[\text{H}^+]}{k_1 + k_3 + k_2[\text{H}^+]} \right) \quad (5)$$

the pH behaviour of Φ_{1a} (Figure). A similar mechanism could also apply to the benzonitrile complex since the very low Brønsted basicity of benzonitrile would make the k_2 step insignificant, leaving $\Phi_{1a} = \Phi_A[k_1/(k_1 + k_3)]$ as the acid independent quantum yield.

Another interpretation of the pH effect is that one of the pathways leading to photoaquation products involves protonation of an electronic excited state. If the protonation leads irreversibly to products, kinetic analysis of this step would be indistinguishable from that for equations

(2)—(4). If the protonation step were a reversible equilibrium, the titration curve shape of the Figure suggests an excited state pK_a of *ca.* 1.5—2.0. Either route has analogy since the thermal (dark) aquations of $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+}$ display pathways first order in $[\text{H}^+]$, an observation tentatively suggested to reflect a rate determining step involving protonation of filled *d*-orbitals.⁴ The organonitrile complexes, $[\text{Ru}(\text{NH}_3)_5(\text{RCN})]^{2+}$, display similar $[\text{H}^+]$ dependent thermal aquation pathways, although the rates² of these pathways are more than an order of magnitude slower than for $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$. Consequently, the data do not exclude protonation of a pyridine complex excited state, since benzonitrile which deactivates the thermal acid catalysed aquation, may also decrease the basicity of the excited state and not show an acid catalysed photoaquation pathway.

Acid concentration effects have been observed for the

photoaquation of polycyano-metallate complexes, but these have been attributed⁵ to equilibrium protonation of the starting material and to protonation of the released cyanide to suppress an efficient back reaction. Addition of pyridine (10^{-4} M) to a neutral or basic photolysis solution does not decrease Φ_{1a} , but enhances it by *ca.* 25%. This observation negates the possibility that the pH effect reflects an efficient back-reaction of $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ with pyridine. Also, significant equilibrium protonation of the ground state is highly unlikely for either the pyridine or benzonitrile complexes since their electronic spectra are invariant over the entire pH range of the photolysis conditions.

We thank the Petroleum Research Fund, the Research Corporation, and the National Science Foundation for support of this research.

(Received, March 11th, 1971; Com. 209.)

¹ P. C. Ford, D. H. Stuermer, and D. P. McDonald, *J. Amer. Chem. Soc.*, 1969, **91**, 6209.

² D. A. Chaisson, unpublished results.

³ R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 227.

⁴ P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, 1968, **7**, 1976.

⁵ S. Ohno, *Bull. Chem. Soc. Japan*, 1967, **40**, 1765.