Formation of Metal Ion–Nitrene Complexes

Sir:

The production of electron-deficient nitrene species *via* the action of ultraviolet light or acid on organic azides is well established.[1,2] The stabilization of nitrenes by coordination to transition metals has been hypothesized,[3] and recently a copper–nitrene intermediate has been proposed in the copper-catalyzed decomposition of benzenesulfonyl azide.[4] However, as yet no well-established case of a metal–nitrene complex has been described. We wish now to report the formation of nitrene coordinated to ruthenium ion *via* the action of acid on ruthenium(III) azide complexes.

The addition of aqueous acid to ruthenium(III) azides causes the vigorous evolution of gas. Mass spectral analysis showed this to be greater than 99% nitrogen. This behavior is markedly different from that of most transition metal azides with acid. In general, acid merely catalyzes the displacement of coordinated azide as hydrazoic acid. For the action of H_2SO_4 on $[Ru(NH_3)_5N_3](N_3)_2$, the products have been characterized from their ultraviolet spectra. Two intense bands were produced at 220 and 262 mμ (Figure 1). Their wavelengths and intensities agree well with those reported for $[Ru(NH_3)_5N_2]^{2+}$ (A) and the dimer $[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}$ (B), respectively.[5] When reaction solutions were made slightly basic the band at 262 mμ gradually decreased in intensity and the band at 220 mμ increased. A sharp isosbestic point was observed at 240 mμ. This latter behavior confirms the assignment of products since Taube, *et al.*, have previously shown that $[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}$ dissociates in weakly basic media into $[Ru(NH_3)_5N_2]^{2+}$ (A) and $[Ru(NH_3)_5OH]^{+}$.[5] Samples isolated from acid solution (as tetraphenylborate salts) at the end of gas evolution were diamagnetic and exhibited strong infrared bands in the region (2100–2200 cm^{-1}) associated with ruthenium(II)–nitrogen complexes. The analyses of these solids corresponded to mixtures of A and B.

Table I. Reaction of H_2SO_4 on $[Ru(NH_3)_5N_3](N_3)_2$ at Room Temperature[a]

Complex concn, *M*	H_2SO_4 concn, *M*	Per cent yield A	Per cent yield B	Total per cent yield (A + B)
9.5×10^{-5}	Water	85	0	85
9.5×10^{-5}	0.05	102	8	110
9.5×10^{-5}	0.15	53	45	98
9.5×10^{-5}	0.40	47	52	99
9.5×10^{-5}	0.80	40	67	107
9.5×10^{-5}	4.0	30	65	95
9.5×10^{-5}	0.80	40	67	107
9.9×10^{-4}	0.80	45	50	95
1.1×10^{-2}	0.80	93	8	101
6.5×10^{-2}	0.80	95	1	95

[a] The most significant features apparent from Table I are: (i) the production of large amounts of $[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}$ (B), (ii) the absence of dimer (B) formation unless acid is present, and (iii) the marked decrease in dimer (B) yield with increasing concentration of $[Ru(NH_3)_5N_3](N_3)_2$.

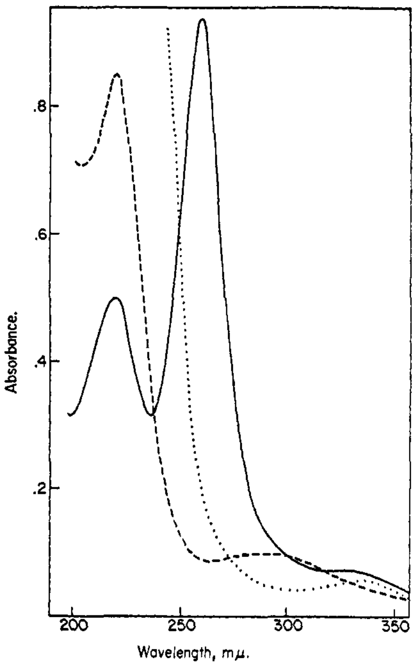


Figure 1. $[Ru(NH_3)_5N_3](N_3)_2$ + 1 *N* H_2SO_4, 7.8×10^{-5} *M* (———); $[Ru(NH_3)_5N_3](N_3)_2$ + H_2O, 9.9×10^{-5} *M* (- - - - - - -); $[Ru(NH_3)_5N_3](N_3)_2$ + 1 *N* H_2SO_4, 7.8×10^{-5} *M*, + 1.90×10^{-4} *M* thiourea (· · · · · · ·).

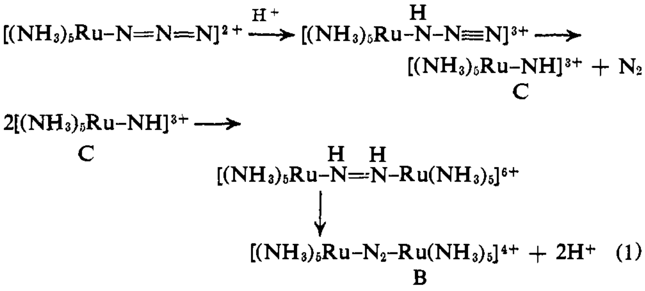
The results of product composition studies on the acid reaction of $[Ru(NH_3)_5N_3](N_3)_2$ are summarized in Table I. In 0.80 *M* H_2SO_4, reaction is complete within 5 min. This rapid appearance of $[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}$ (B) eliminates the possibility that it is produced by the combination of $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$. The rate of the latter reaction has been measured by Itzkovitch and Page.[6] Under the conditions employed here, such combination would require several hours.

The vigorous evolution of nitrogen and the rapid formation of nitrogen-bridged dimers are very reminiscent of the behavior of organic azides when treated with acid or ultraviolet radiation.

$$Ph{-}N_3 \xrightarrow{h\nu} Ph{-}N + N_2$$

$$Ph{-}N + Ph{-}N \longrightarrow Ph{-}N{=}N{-}Ph$$

We believe a similar pathway involving a metalated nitrene (C) is present in the acid reaction of $[Ru(NH_3)_5N_3]^{2+}$ (eq 1). Strong support for the presence



$$[(NH_3)_5Ru{-}N{=}N{=}N]^{2+} \xrightarrow{H^+} [(NH_3)_5Ru{-}\overset{H}{N}{-}N{\equiv}N]^{3+} \longrightarrow \underset{C}{[(NH_3)_5Ru{-}NH]^{3+}} + N_2$$

$$2\underset{C}{[(NH_3)_5Ru{-}NH]^{3+}} \longrightarrow [(NH_3)_5Ru{-}\overset{H}{N}{=}\overset{H}{N}{-}Ru(NH_3)_5]^{6+} \longrightarrow \underset{B}{[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}} + 2H^+ \quad (1)$$

of the nitrene intermediate (C) was obtained from trapping experiments. In the presence of small

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(5) D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1967).

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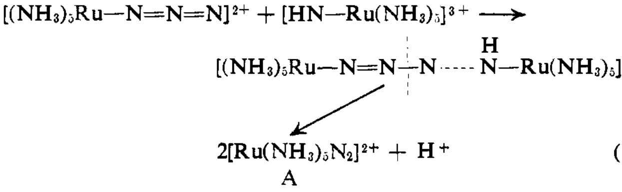
amounts of thiourea, diethyl sulfide, or I^-, the reaction of acid on $[Ru(NH_3)_5N_3](N_3)_2$ generated no dimer (B) (see Figure 1). This behavior may be readily rationalized in terms of the Lewis acid character of $[(NH_3)_5Ru-NH]^{3+}$ (C). Coordinated nitrene, like the similar carbene, is expected to be a soft acid.[7] Combination of $(NH_3)_5Ru-NH$ with itself to produce the dimer (B) is quenched by the more rapid reaction of the nitrene with the soft bases thiourea, $(C_2H_5)_2S$, or I^-. On the other hand, reagents such as Cl^-, PF_6^-, CH_3CN, or dimethyl sulfoxide had no observable effect on the course of the acid reaction.

The decrease in yield of the dimer (B) with increasing initial concentration of $[Ru(NH_3)_5N_3](N_3)_2$ (Table I) suggests that $[Ru(NH_3)_5N_3]^{2+}$ may also function as an effective trap for the nitrene (C) (eq 2). A combination of eq 1 and 2 explains the production of both A and B in the acid reaction of $[Ru(NH_3)_5N_3]^{2+}$.



$$[(NH_3)_5Ru{-}N{=}N{=}N]^{2+} + [HN{-}Ru(NH_3)_5]^{3+} \longrightarrow [(NH_3)_5Ru{-}N{=}N{-}N\cdots\overset{H}{N}{-}Ru(NH_3)_5]^{5+} \longrightarrow \underset{A}{2[Ru(NH_3)_5N_2]^{2+}} + H^+ \qquad (2)$$

The behavior of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ and *cis*-$[Ru(trien)(N_3)_2]PF_6$ in acid is very similar to that of $[Ru(NH_3)_5N_3](N_3)_2$. The final spectra again exhibited two intense bands at 221 and 264 mμ. The band at 221 mμ agrees well with the known spectrum of *cis*-$[Ru(en)_2N_2H_2O]^{2+}$ (A′).[8] The bands at 264 mμ have been assigned to the dimers $[(A{-}A)_2H_2ORu{-}N_2{-}RuH_2O(A{-}A)_2]^{4+}$ (B′) (A–A = en, 0.5 trien). The latter compounds have been independently prepared *in situ*, and their spectra ($\epsilon_{264} = 48{,}000$) agree closely with that reported for $[(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+}$.[5] The presence of small amounts of thiourea or I^- in the acid reactions again eliminated the formation of the dimers (B′), supporting the presence of reactive nitrene intermediates.

Attempts to observe an esr signal for the postulated nitrene intermediates have been unsuccessful. Solutions of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ (0.038 *M*) in H_2SO_4 (0.80 *M*) were frozen in liquid nitrogen after various reaction times, and their esr spectra recorded. All resonances observed in the region 1000–8000 G have been assigned to the unpaired electron of ruthenium(III). These bands decreased with increasing reaction time due to the formation of ruthenium(II). The failure to observe a nitrene resonance suggests it may be present in a singlet electronic state, though it may also be due to a low nitrene concentration.

A search has been made for similar acid-catalyzed behavior among other transition metal azide complexes. Azide complexes of Co(III), Rh(III), Pt(II), Pd(II), and Au(III) generated no gas when dissolved in 4 *M* H_2SO_4 at room temperature. However, similar behavior has been found in these laboratories for the Ir(III) complex *trans*-$[Ir(en)_2(N_3)_2]PF_6$.[9] Ultraviolet irradiation of metal azide complexes appears to be an alternative source of metalated nitrenes.[10]

Compounds such as $ReCl_3(P(C_2H_5)_2C_6H_5)_2NC_6H_4X$ are known and their structures have been determined.[11] While these may formally be considered as arylnitrenes coordinated to metal ions, they are very stable and are best formulated as arylimino complexes.[12]

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A Model for the Interaction of Cytochrome P-450 with Carbon Monoxide[1]

Sir:

Although P-450 cytochromes are hemoproteins containing protoporphyrin IX, many of their spectral properties are exceptional for hemoproteins. In particular, the reduced P-450–CO complex shows a Soret peak at 450 mμ,[2] while the reduced P-450–ethyl isocyanide complex shows a pair of Soret peaks at 428 and 455 mμ.[3]

P-450 is converted to a modified form, P-420, by the action of organic solvents, detergents, or certain enzymes.[4] These modifications remove the anomalous spectral properties of the reduced cytochrome, and thus P-420 shows spectral properties of a typical *b*-type cytochrome (CO complex λ_{max} 421, 538, 565 mμ).

Since P-450 cytochromes of mammalian origin are tightly bound to cellular membranes, a separation from lipids and other components of membranes has not been achieved without accompanying conversion to P-420. For this reason, model compounds are particularly useful in understanding the anomalous spectral characteristics of P-450.

Imai and Sato[5] have recently shown that ethyl isocyanide can form a complex with protoheme in which the 455-mμ Soret peak of the reduced P-450–ethyl isocyanide is reproduced. They have shown that this unusual protoheme complex requires an association of two or more protohemes. Consequently, they suggest that the anomalous spectral properties of reduced P-450 complexes are due to a direct interaction of two hemes. However, no evidence has been provided about possible interaction of two hemes in the corresponding CO complex of either reduced protoheme or P-450.

Several years ago, Holden and Lemberg[6] reported that the complex of reduced protoheme, pyridine, and CO showed a Soret peak at 440 mμ. When this work was repeated, we found that the visible absorption

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