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Ruthenium Nitrosyl Complexes from Solutions of Ruthenium(III) Ammines in Dilute Perchloric Acid

Sir:

Unknown brown-black solutions have been reported when dilute perchloric acid reacts with the chloropentaammineruthenium(III) cation.[1] We now find that nitrosyl complexes of ruthenium may be isolated from such solutions, the NO group being readily identified by its characteristic infrared absorption spectrum.

At steam-bath temperatures, reaction between the metal complex (concentration $\sim 10^{-3}$ *M*) and 0.1 *M* perchloric acid is evident by the marked color development after approximately 10 min. After a further 2 hr deep purple solutions are obtained, and by slow (48 hr) fractional crystallization on the steam bath both purple-black and yellow solids may be isolated. The infrared spectrum of the yellow product in potassium bromide has the following bands (cm^{-1}) for which assignments are given in parentheses: 3500 br s (H_2O), 3220 s, 3120 s (N-H), 1850 s (N-O), 1620 br w (N-H, H_2O), 1300 m (N-H), 1140 s, 1120 s, 1080 s, 940 w (ClO_4^-), 840 br m (N-H) (br = broad; s = strong; m = medium; w = weak). This spectrum agrees with that reported for the $[RuOH(NH_3)_4NO]^{2+}$ cation with the inclusion of the ClO_4^- modes.[2,3] The less-soluble purple-black fractions showed a strong absorption at 1925 cm^{-1} in addition to the above list. This is attributed to the presence of some $[RuH_2O(NH_3)_4NO](ClO_4)_3$ for which frequencies are expected in the 1910–1920-cm^{-1} region, the exact location depending upon the counterion.[4] The intense dark colors of the solutions and certain of the solids isolated are no doubt due to chloronitrosyl complexes. Thus, from the more soluble fractions, solids having strong additional absorption at 1880 cm^{-1} are obtained. Also, decomposition of the purple solids with sodium hydroxide followed by acidification and treatment with silver nitrate shows the presence of chloride ion.

When a chloride-free preparation of $[RuH_2O(NH_3)_5](ClO_4)_3$ is used in these experiments, chloride ion may be detected among the reaction products. Hexaammineruthenium(III) chloride also reacts with 0.1 *M* perchloric acid when heated in solution on the steam bath to yield nitrosyl complexes. For similar concentrations of reagents, the reaction is distinctly slower than for the pentaammine complexes, suggesting that coordination of ClO_4^- may be the initial step in this unusual reaction.

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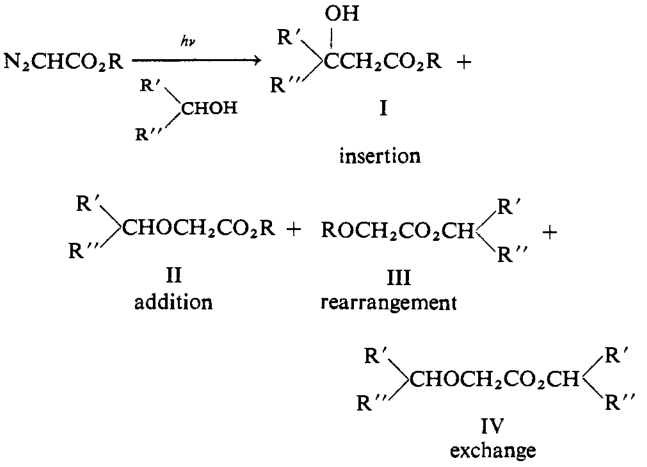
Photochemistry of Diazo Esters. II. A Novel Reaction Path

Sir:

Photolysis of diazo compounds is generally assumed to proceed by a carbene mechanism.[1-3] Our current study on a series of diazoacetates in alcohols, however, indicates a novel reaction path not involving carbene intermediates.



Products I, II, and III have been rationalized in terms of carbalkoxymethylene reactions.[2-4] The formation of IV, with a net exchange of the alcohol moiety, is the main concern of the present communication. The reaction is quite general since exchange products were found in each system studied (Table I), and the exchanged alcohol could also be detected. The efficiency of exchange varies with respect to substituents in the order PhO $\simeq$ MeO > EtO > *i*-PrO $\simeq$ AllylO $\simeq$ *t*-BuO, and with respect to the solvent, Me < Et < *i*-Pr < *t*-Bu alcohol. Evidently steric effects are not important, and all esters exchange freely in *t*-butyl alcohol; moreover, the *t*-butyl ester solvolyzes as readily as its isopropyl and allyl analogs.

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