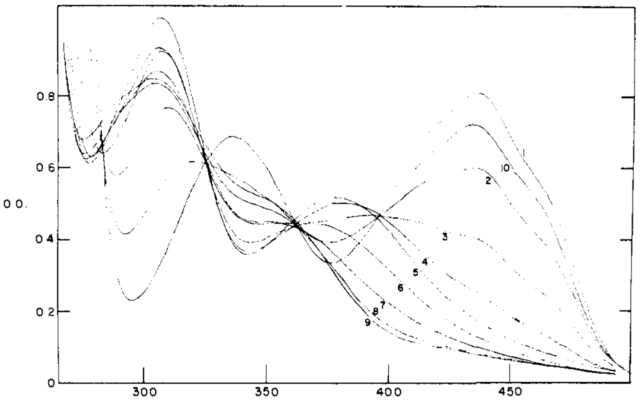

Figure 1. Photolysis of II (8 × 10^{-5} *M*) in the presence of EDTA (0.01 *M*) at pH 6.4. Traces 2 and 3 were recorded after 2 and 5 min of photolysis (total time); curves 4–9 were taken after an additional 0.1, 0.5, 1.5, 3.0, 5.0, and 8.0 hr of photolysis, respectively; curve 10 was traced after the admittance of air after prolonged photolysis. Initial sample contained in a 1-cm Thunberg cuvette was deoxygenated by alternatively evacuating and admitting V^{2+}-deoxygenated argon 20X. The photolysis was carried out with a No. 1 BBA floodlight at a distance of 6 in. The cuvette was kept at 25° in a water bath.

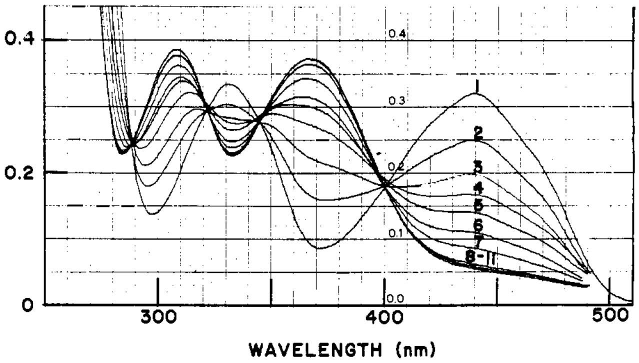

Figure 2. Photolysis of IV (3.5 × 10^{-5} *M*) in the presence of EDTA (0.01 *M*) at pH 6.4. Curve 1 was taken after deoxygenation (see caption, Figure 1); curves 2–10 were taken after 0.25, 0.5, 0.75, 1.0, 1.75, 2.75, and 7.75 min of photolysis (total time), respectively; curve 11 was taken after an additional 1 hr of photolysis and is identical with 8 below 400 nm. Photolysis was at 25° with a 100-W bulb at a distance of 6 in.

the characteristic spectra of a 4a adduct.[5,7] Photolysis of I and III in the presence of EDTA (0.01 *M*, pH 6.1, V^{2+}-scrubbed argon atmosphere) results in their direct conversion to the corresponding 1,5-dihydroisoalloxazines without the appearance of intermediates. In Figure 1 is presented the spectral time course for the photolysis of II in the presence of EDTA. Examination of the figure reveals that initial photolysis is associated with fairly tight isosbestic points (395, 362, 325, and 283 nm) which then break upon further irradiation. Spectra taken at intermediate times during the photolysis, *e.g.*, spectrum 5, show λ_{max} at 376 and 307 nm, which is in agreement with that for other 4a adducts.[5,6] Admittance of air at this point gave a 98% return of II_{ox} based on λ_{max} at 435 nm. This observation is noteworthy in that other 4a adducts have required illumination in the presence of O_2 to restore oxidized flavines.[5] Prolonged photolysis, shown in spectra 6–9, resulted in a decrease in absorbance at 376 and 307 nm and the appearance of a shoulder at 288 nm, characteristic of 1,5-dihydroflavine. Admittance of air at this point gave a 89% return of II_{ox} showing some irreversible photolysis of the isoalloxazine nucleus. These results are consistent with an A → B → C process. Much the same results were obtained when EDTA was replaced by phenylacetic acid which has previously been established to form 4a-addition products with flavines on photolysis.[6] In this case tight isosbestic points were obtained initially at 386, 361, and 321 nm which broke away on continued photolysis to yield a spectrum consistent with the production of reduced flavine. However, admittance of air provided only a 58% return of II_{ox}. The course of photolysis of IV in the presence of EDTA is shown in Figure 2. Examination of Figure 2 reveals that the spectrum of IV gives way to that anticipated of a 4a adduct with isosbestic points at 400, 345, 322, 288, and 266 nm. With prolonged illumination of the reaction mixture the 4a adduct failed to provide a species exhibiting the spectra of reduced flavine. Admittance of air regenerated IV_{ox} in ~99% yield.

The present results establish that photoreduction of isoalloxazines with EDTA in aqueous solution may yield, depending on the isoalloxazine, an intermediate, the spectra of which suggest a 4a adduct. Further, the stability of the 4a adduct would appear to be a function of electronic and possibly steric factors. Thus, when H occupies the 6, 7, and 8 positions (I) or when there is a CN group at the 7 positon (III) no intermediate may be discerned on the path of photoreduction. Sulfonic acid substituents at the 6 and 8 positions (II) allow observation of the formation and photolysis of an intermediate while an 8-cyano group (IV) provides a stable 4a adduct which does not go on to 1,5-reduced isoalloxazine. Electron withdrawal by a substituent at the 8 position would thus appear to stabilize the adduct. These results do not differentiate between the two possibilities that: (1) EDTA photoreduction proceeds solely through a 4a adduct and (2) two mechanisms of EDTA photoreduction compete so that electron-deficient isoalloxazines are reduced *via* 4a-adduct intermediates while non-electron-deficient isoalloxazines are directly reduced to the 1,5 dihydro structure. In progress is an extensive study of the photocatalytic reaction of variously substituted isoalloxazines with EDTA. Our objective is the elucidation of the controlling structure–function relationships.

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Intramolecular Rearrangement of Pentacoordinate Nitrosyl Complexes

Sir:

Correlation of the MNO angle with coordination geometry for five-coordinate metal nitrosyl complexes is

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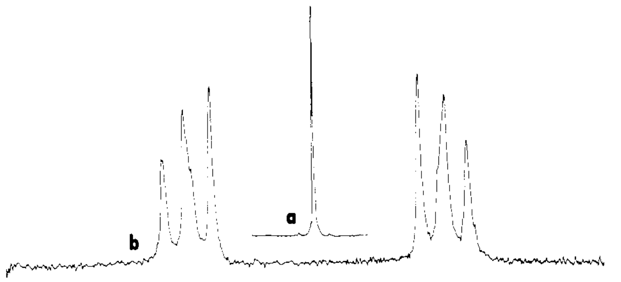


Figure 1. White-noise proton-decoupled ^{31}P spectrum of FeNO(diphos)$_2^+PF_6^-$ in acetone-d_6 at 30° (a) and −85° (b).

presently under intensive study.[1] There has evolved an empirical generalization that linear MNO groups exist in trigonal bipyramidal complexes while bent (120–140°) MNO groups occur only in square-pyramidal environments. Evidence has been presented suggesting that linear and bent MNO moieties may in some cases coexist and interconvert rapidly.[2] In view of the generally facile interconversion of square-pyramidal and trigonal-bipyramidal frameworks,[3] a study of the energetics of this rearrangement in five-coordinate nitrosyl complexes is expected to provide insights into the origin of their catalytic ability. We communicate here the first detailed mechanistic information concerning pseudorotation in five-coordinate nitrosyls.

The white-noise proton-decoupled ^{31}P nmr spectrum of FeNO(diphos)$_2^+$ [4] at room temperature (Figure 1a) consists of a singlet with δ −81.5 ppm (positive shifts are upfield of external 85% H_3PO_4). Since the related complex RuNO(diphos)$_2^+$ is known[5] to be trigonal bipyramidal with equatorial NO, time averaging is implied by this spectrum. Lowering the sample temperature produces a complex sequence of changes in the ^{31}P spectrum until, at −85° in acetone-d_6, the pattern shown in Figure 1b is observed. This AA′BB′ pattern is consistent with the solid-state structure of Ru(NO)(diphos)$_2^+$. Approximate spectral parameters are $J_{\mathrm{P_{ax}-P_{eq}}} = 12$ Hz, $J_{\mathrm{P_{ax}-P'_{eq}}} = 57$ Hz, and $\delta\nu = 369$ Hz (at 40.5 MHz). RuNO(diphos)$_2^+$ exhibits the same temperature-dependent phenomena and, at −100°, $J_{\mathrm{P_{ax}-P_{eq}}} = 27$ Hz, $J_{\mathrm{P_{ax}-P'_{eq}}} = 22$ Hz, and $\delta\nu = 62$ Hz. The spectral behavior is entirely reversible with temperature, is independent of solvent ($CHCl_3$, $CHClF_2$, or acetone), and is unaffected by addition of diphos or $PMePh_2$. The ^{31}P spectrum of the new complex RhNO(diphos)$_2$(PF$_6$)$_2$ at 30° is a sharp doublet with $J_{\mathrm{Rh-P}} = 115$ Hz. Intramolecular exchange of axial and equatorial phosphorus nuclei accounts for all of these observations. The activation energies decrease in the order Fe > Ru.

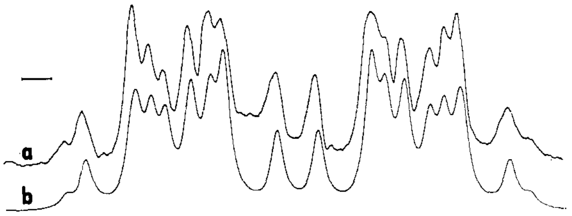
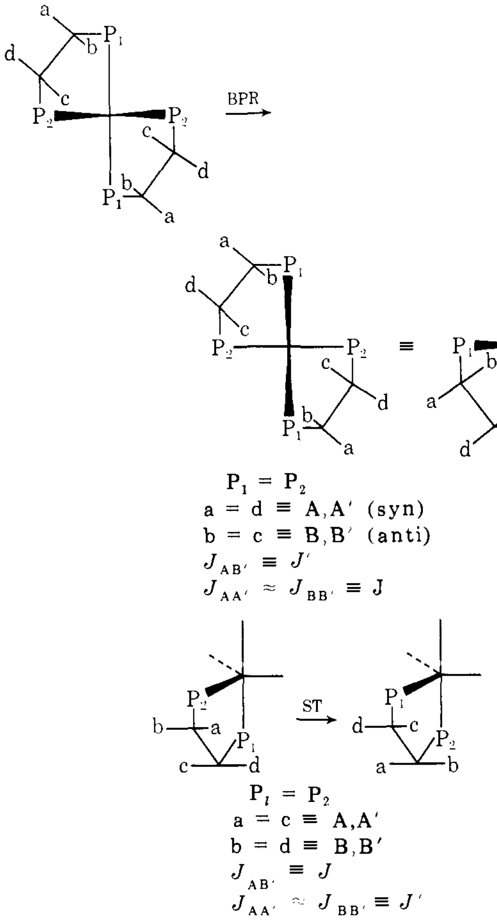


Figure 2. Experimental (a) and calculated (b) ^{31}P decoupled 220-MHz methylene proton spectrum of RuNO(dipos)$_2^+PF_6^-$ in acetone-d_6 at 15°. Horizontal bar indicates 5 Hz.

Scheme I



Mechanistic analysis in terms of "basic permutational sets" yields two permutationally distinct methods for equilibrating axial and equatorial positions.[6] These are shown in Scheme I and correspond to (among others) the physical processes of (1) twisting a single MP_2C_2 ring 180° about a line from M to the C–C midpoint ("single twist," ST) and (2) turnstile rotation or Berry pseudorotation (BPR). Total ^{31}P line shape calculations for the two permutational sets show them to be spectroscopically indistinguishable in the molecules studied here.

Differentiation between ST and BPR permutations is possible, however, by analysis of the ^{31}P-decoupled proton nmr of the methylene protons in the region of rapid exchange. ^{31}P decoupling converts the broad, relatively featureless spectrum of the methylene protons of RuNO(diphos)$_2^+$ into a symmetric pattern characteristic of an AA′BB′ spin system (Figure 2). Least-squares refinement yields the following parameters (in Hz):[7] $\delta\nu_{AB} = 40.3$, $J_{AB} = -14.3$, $J_{AA'} = 6.3$, $J_{AB'} = 8.0$, $J_{BB'} = 6.2$.

The magnitude and unique sign of J_{AB} identifies A and B as a geminal pair, a feature common to ST and BPR. The mechanistic information carried by the

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proton resonances is based on the fact that BPR maintains the syn and anti relationship of methylene protons with respect to NO. The ST permutation does not show this behavior (Scheme I), and it is thus possible to identify the permutational sequence responsible for the rearrangement. The necessary structural information can be extracted from an analysis of the vicinal proton–proton coupling constants using the Karplus equation. It is first necessary to average $^3J_{HH}$ over the two rapidly equilibrating[8] conformations of the puckered five-membered ring; this yields two values, $J = J(\varphi)$ and $J' = {}^1/_2[J(120 + \varphi) + J(120 - \varphi)]$ where φ is the dihedral PCCP angle. Karplus equation parameters appropriate to coordinated ethylenediamine[9] show that J is smaller than J' by $\sim$2 Hz. BPR predicts a pattern of two J (small) and one J' (large), while ST would show just the opposite pattern. The actual pattern is in agreement only with BPR, a simultaneous motion of two axial and two equatorial phosphorus nuclei.

It is evident that BPR interconverts enantiomers while ST does not. We have attempted to confirm our assignment of BPR by determining whether enantiomerization and axial–equatorial interchange occur at identical rates using ^{31}P nmr in the presence of chiral shift reagents.[10] However, the low basicity of the nitrosyl oxygen combined with the limited solubility of $RuNO(diphos)_2BPh_4$ in $CHCl_3$ makes complex formation negligible; the ^{31}P resonance is unaffected by shift reagents.

If the permutational sequence which occurs in these complexes proceeds by a Berry physical pathway, the transition state is a square pyramid with NO axial. Bending of the MNO angle may therefore accompany pseudorotation and have an observable effect upon the activation energy. We are attempting to assess the importance of this effect by studying the energetics of pseudorotation in other complexes of the type $ML(diphos)_2$, L = NO and CO.

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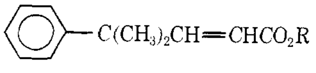
Mechanisms of Photochemical Reactions in Solution. LXXVI.[1] Complex Decay Mechanisms in Bi- and Trichromophoric Systems

Sir:

Bichromophoric molecules, in which the chromophoric units are not directly conjugated, have been studied extensively by photochemists and spectroscopists.[2–19] Appearance of new, red-shifted emission[20–22] and accelerated nonradiative decay by both chemical and nonchemical paths give evidence for decay of excited states by way of low-lying states involving excitation delocalization over the two chromophoric units, even when absorption spectra show no significant evidence for interchromophoric coupling in excitation.

Although bichromophoric systems are far from understood, we have begun to probe the behavior of "polychromophoric" molecules in which three or more chromophoric units are potentially capable of participating in excitation delocalization. We wish to report the behavior of the bichromophoric system **1** and that of trichromophoric molecules **2** and **3** in which aliphatic and aromatic amino functions have been added as third chromophoric units.


$C_6H_5C(CH_3)_2CH{=}CHCO_2R$

1, R = C_2H_5
2, R = $CH_2CH_2N(CH_3)_2$
3, R = $CH_2CH_2N(CH_3)C_6H_5$

All three systems consist of cis and trans isomeric pairs. The trans isomers were prepared by standard synthetic methods in which the key step was addition of the anion derived from diethyl carbethoxymethylphosphonate to phenyldimethylacetaldehyde.[23] In all cases irradiation led to trans → cis isomerization and in some cases other changes (*vide infra*). The cis isomers were then isolated by vapor chromatography. The compounds were characterized by nmr and uv spectra.

The absorption spectra of *cis*- and *trans*-**1** were similar to that of cumene in the 260-nm region but with small red shifts and small increases in total intensity. In both cases there is much stronger absorption in the region below 250 nm which does not reach a maximum above 210 nm. The latter feature qualitatively resembles the spectrum of ethyl crotonate but with a

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