assigned by comparison with the reported spectrum of **2c**[3b] in which the assignments of methyl resonances are unambiguous by integration. Thus, the mixture of **8c** and **8d** exhibited two methyl resonances at δ 2.41 (s) (relative intensity 1.0) and at δ 2.09 (s) (relative intensity 1.4). The higher field, higher intensity, methyl resonance must be that in the isomer with the methyl group in the terminal position of the η^3-allyl portion of the cyclobutenonyl ligand, i.e., **8d**. The corresponding ring proton resonances are δ 4.84 (s) (**8c**) and δ 5.15 (s) (**8d**).
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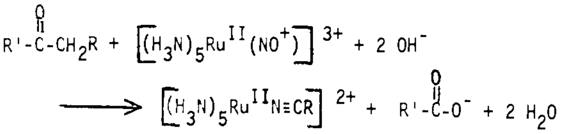
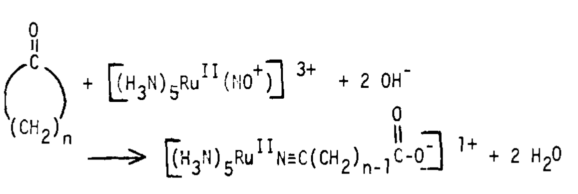
Reaction of Nitrosylpentaammineruthenium(II) Ion with Organic Carbonyls Containing an α-Methylene Group: Facile Oxidative Cleavage of a Carbon-Carbon Bond

Sir:

We report the facile oxidative cleavage of ketones (and aldehydes) by the action of nitrosylpentaammineruthenium(II) ion in dilute aqueous base. The stoichiometries shown in eq 1 and 2 have been established for open chain compounds (**1**) and for cyclic ketones (**2**).


$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2R + [(H_3N)_5Ru^{II}(NO^+)]^{3+} + 2\ OH^- \longrightarrow [(H_3N)_5Ru^{II}N{\equiv}CR]^{2+} + R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- + 2\ H_2O \quad (1)$$

where R = alkyl or phenyl and R' = H, alkyl, or phenyl


(2)

where n = 4, 5 or 6.

The only ruthenium-containing products are nitrilepentaammineruthenium(II) species, which are isolated as perchlorate salts and identified by comparing infrared and electronic spectra with those in the literature.[1,2] Table I lists some typical carbonyl compounds which have been used, the nitrile products, and their yields. In those cases in which the organic compound dissolves completely in 0.1 M NaOH, the reaction appears to be complete within 10 min at room temperature. The benzoate ion has been identified as a major reaction product in the reaction with $C_6H_5CH_2C(O)C_6H_5$ as substrate by conversion to benzoic acid and identification via infrared, NMR, and melting point. The products from the reactions with cyclic ketones exhibit, as expected, infrared peaks distinctive for both nitrile and carboxylic acid functions.

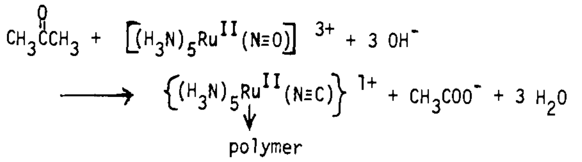
A reaction also occurs with compounds containing α-methyl but no other α-hydrogen atoms (e.g., acetone and acetaldehyde). These reactions produce intractable products as would be expected from the known chemical behavior of the cyanopentaammineruthenium(II) ion.[3] Reaction 3 thus provides on alternative to the haloform reaction.

When *both* methyl and methylene groups are present (e.g., 2-butanone) the reaction occurs predominantly at the methylene carbon. Decreasing the pH to 7 stops the reaction as does increasing OH^- to 2 M (which is known to convert the nitrosyl ligand to nitrite[4]).

Table I. Typical Results with Compounds Containing α-Methylene Groups

carbonyl	nitrile product $(H_3N)_5RuN{\equiv}CR^{2+}$, R	% yield[a]
CH_3CH_2CHO, propanal	CH_3	67
$CH_3CH_2C(O)CH_2CH_2$, 2-pentanone	CH_3	55
$CH_3CH_2C(O)CH_3$, 2-butanone	CH_3	79
$C_6H_5CH_2CHO$,[b] phenylacetaldehyde	C_6H_5	49
$C_6H_5CH_2C(O)C_6H_5$,[b] benzyl phenyl ketone	C_6H_5	44
$CH_2{=}CHCH_2CH_2C(O)CH_3$,[b] 5-hexen-2-one	$CH_3CH{=}CH$[c]	23
$\overline{CH_2(CH_2)_5C}{=}O$,[b] cycloheptanone	HOOC-$(CH_2)_4CH_2$[d]	87

[a] Based on weight of recrystallized perchlorate salts. [b] Limited solubility in 0.1 M NaOH. [c] Note that the double bond undergoes *base-catalyzed* isomerization into a conjugated position. [d] Acidified before perchlorate addition.

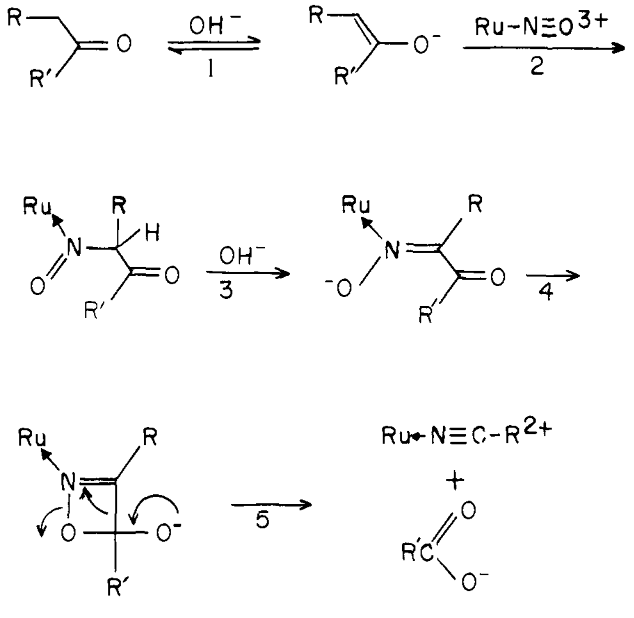

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + [(H_3N)_5Ru^{II}(N{\equiv}O)]^{3+} + 3\ OH^- \longrightarrow \underset{\substack{\downarrow\\ \text{polymer}}}{\{(H_3N)_5Ru^{II}(N{\equiv}C)\}^{1+}} + CH_3COO^- + 3\ H_2O \quad (3)$$

Most of the previously reported reactions of the $Ru^{II}NO^{3+}$ moiety have involved nitrogen containing species such as hydrazine,[5] hydroxylamine,[5] azide,[6] aromatic[7] and aliphatic[8] amines, and coordinated amido ligands[8,9] to form new nitrogen-nitrogen bonds, although formation of N-coordinated nitroso[10,11] and oxime[12,13] complexes have also recently been noted.[14] This report represents the first case in which a carbon-nitrogen triple bond is formed and in which a carbon-carbon bond is cleaved by the reaction of $Ru^{II}NO^{3+}$ or any other metal nitrosyl species.

The mechanism in Scheme I is postulated.[15]

The driving forces for the above reaction are the formation of a CO_2^- chromophore, the high electrophilicity of the NO^+ ligand,[16] and the well-established stabilization of Ru(II) complexes by π-acceptor ligands such as nitriles via dπ-pπ* back-bonding.[17]

Scheme I



Work is in progress to establish the generality of this reaction for use in organic synthesis. Thus, it is observed that a facile reaction also occurs with compounds containing a single α hydrogen, although it has not yet been possible to isolate the major reaction products. Previous studies have demonstrated that aldehydes and ketones with no α hydrogens undergo an entirely different (and much slower) reaction involving the ammonia ligand trans to the nitrosyl group.[18]

The most apparent synthetic potential of reactions 1 and 2 is for oxidative ring opening and bifunctionalization of cyclic ketones under very mild conditions, thus representing an excellent alternative to present oxidative cleavage methods such as Marshall's[19] cleavage of α-diketone monothioketals or the known oxidative cleavage of cyclic olefins[20] for the synthesis of macrocyclic compounds or compounds containing linear chains with fixed stereochemistry.

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(15) Support for this mechanism is provided by (a) the isolation of oximes in many of the analogous nitroprusside reactions[14] and (b) our observation of the formation of a nitrile ruthenium species in the reaction of $(H_3N)_5RuOH_2^{2+}$ with diacetyl monoxime, presumably by the reaction sequence $(H_3N)_5RuOH_2^{2+} \rightarrow (H_3N)_5RuN(OH){=}C(CH_3)C(O)CH_3^{2+} \rightarrow (H_3N)_5RuN{\equiv}CCH_3^{2+}$ + other products.
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Luminescent Photoelectrochemical Cells. Use of Tellurium-Doped Cadmium Sulfide Photoelectrodes to Probe Surface Recombination during the Conversion of Optical Energy to Electricity

Sir:

Photoelectrochemical cells (PECs) consisting of an illuminated n-type semiconductor photoelectrode, a Pt counterelectrode, and a suitably chosen electrolyte have been used to convert optical energy directly into electricity.[1-8] Improvement of PEC efficiencies requires an understanding of the excited-state properties of semiconductor electrodes and, in particular, the extent to which they can be manipulated by experimental parameters. Thus far, attention has focussed on *nonradiative* deactivation leading to electrochemistry and, more specifically, on the role of the electrolyte in determining whether oxidation of the electrode and/or the electrolyte occurs.[1-9] Studies of *radiative* deactivation involving semiconductor electrodes have been largely confined to transient electroluminescent phenomena.[10,11]

We now report that PECs employing n-type, Te-doped CdS (CdS:Te) photoanodes provide a sensitive probe of the manner in which the semiconductor excited state partitions input optical energy. Photoelectrochemical events are presumed to result from separation of a photogenerated conduction band electron and valence band hole, a consequence of the band bending which characterizes the depletion region created by the semiconductor-electrolyte interface.[12] *The observation of emission in an operating PEC signifies that radiative recombination of electron-hole pairs occurs in direct competition with nonradiative separation leading to electrochemistry.* We demonstrate herein that this competition is sensitive to a PEC parameter which affects band bending, the electrode potential.

Vapor-grown, n-type CdS:Te single crystals are well characterized and are known to luminesce at room temperature upon ultraband gap excitation;[13] the band gap of CdS:Te is at most that of undoped CdS, 2.4 eV.[14] Samples of melt-grown, polycrystalline CdS:Te (5–100 ppm Te) used in this study were etched in concentrated HCl prior to use and exhibit both orange emission (band maximum ~600 nm) and photocurrent at 298 K upon excitation at $\lambda \lesssim 520$ nm.[15] The emission has been ascribed to radiative recombination of excitons trapped at Te atoms which presumably substitute at S sites.[13]

In order to study CdS:Te emissive properties in the PEC, the cell was assembled in the compartment of a spectrophotofluorometer. A 3-mm-diameter Ar ion laser beam was used to excite CdS:Te electrodes positioned at ~45° to both the incident beam and the emission detection optics. Excitation anywhere on the CdS:Te surface causes the entire electrode to emit, since emitted light is not appreciably absorbed by CdS:Te. A Pt foil counterelectrode, an SCE, and electrolytes of sulfide (1 M OH^-/1 M S^{2-}) or polysulfide (1 M OH^-/1 M S^{2-}/0.2–1.0 M S) complete the PEC whose electrochemistry is essentially that of undoped CdS-based PECs.[1-5] That is, oxidation of (poly)sulfide electrolytes competitively precludes the photoanodic decomposition reaction

$$\mathrm{CdS} \xrightarrow{h\nu} \mathrm{Cd}^{2+} + \mathrm{S} + 2e^- \tag{1}$$

observed in OH^- electrolyte. Reduction of polysulfide species at Pt permits sustained optical to electrical energy conversion, since no net change in electrode or electrolyte composition occurs. We observe minimal weight loss or surface damage for CdS:Te even when sufficient photocurrent is passed to have yielded measurable decomposition.[16] Under sustained PEC operation the emission spectrum is unaltered, although we do see both declining photocurrent (similar to that reported for the undoped CdS[1,2]) and emission intensity.

But for intensity differences, the emission spectrum of the CdS:Te electrode from 540 to 800 nm (bandwidth 5 nm) is independent of Ar ion excitation wavelengths (457.9 to 514.5 nm), electrode potential (−0.1 V vs. SCE to the onset of cathodic current),[17] and the composition or presence of (poly)sulfide electrolytes. The crucial result is presented in Figure 1 for 488.0-nm excitation. Increasingly negative bias, corresponding to diminishing band bending within the depletion region, is shown to increase luminescence by up to ~40% as the photocurrent declines to zero. The same effect is noted in sweeping this potential region; we observe that 10 consecutive scans at 100 mV/s are reproducible to within 5%. Excitation at 457.9, 488.0, and 501.7 nm in (poly)sulfide electrolytes

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