and is obtained by He(I) photoelectron spectroscopy.[6] These energetics are also directly related to the electrochemical one-electron oxidation potentials of R_4Pb and the frequencies of the charge-transfer bands of R_4Pb–TCNE complexes are given by ν_{CT}.[6,7]

The rates of insertion of TCNE into R_4Pb also show in Figure 1 a striking correlation with the rates of oxidative cleavage of R_4Pb by hexachloroiridate(IV), in which previous studies demonstrated that the process is rate-limited by the electron-transfer step in eq 4.[6]

$$R_4Pb + Ir^{IV}Cl_6^{2-} \longrightarrow Ir^{III}Cl_6^{3-} + R_4Pb\cdot^{+} \qquad (4)$$

For the insertion reaction, a similar rate-limiting process is given by the electron transfer mechanism in eq 1b, in which TCNE functions as an π-electron acceptor. Indeed, the characteristic visible absorption spectrum[8a] of TCNE$\cdot^-$, as well as its electron spin resonance spectrum[8b] can be readily observed during the reaction of tetraethyllead and TCNE (Figures 2a and b).[9] The subsequent fast transfer of the alkyl group from $R_4Pb\cdot^+$ to TCNE$\cdot^-$ is probably a cage process and occurs by transfer of either R$\cdot$ or R$^+$ as given in eq 5a or 5b, respectively:

$$\begin{tikzcd}
 & {[R\text{–}TCNE^- \ R_3Pb^+]} \arrow[dr] & \\
{[TCNE\cdot^- R\text{–}PbR_3\cdot^+]} \arrow[ur, "a"] \arrow[dr, "b"'] & & III \quad (5) \\
 & {[R\text{–}TCNE\cdot \ R_3Pb\cdot]} \arrow[ur] &
\end{tikzcd}$$

Selectivity studies with a series of mixed methyl-/ethyllead compounds in Table I show that an ethyl group is preferentially transferred, consistent with a weaker Et–Pb bond compared to a Me–Pb bond in eq 6 (where R = methyl or ethyl).[10,11]

$$\begin{tikzcd}
 & Et(NC)_2CC(CN)_2PbR_2(Me) \\
{\overset{Me}{\underset{Et}{>}}PbR_2 + TCNE} \arrow[ur, "k_{Et}"] \arrow[dr, "k_{Me}"'] & \\
 & Me(NC)_2CC(CN)_2PbR_2(Et)
\end{tikzcd} \qquad (6)$$

We favor the mechanistic route represented in eq 5a since a similar selectivity (k_{Et}/k_{Me}) was found in the oxidative cleavage of R_4Pb with $Ir^{IV}Cl_6^{2-}$ (compare eq 4, 7 and 8).

$$RPbR_3\cdot^{+} \xrightarrow{fast} R\cdot + R_3Pb^{+} \qquad (7)$$

$$R\cdot + IrCl_6^{2-} \xrightarrow{fast} RCl + IrCl_5^{2-} \qquad (8)$$

The selectivity is associated with the facile fragmentation of the cation-radical in eq 7 subsequent to the slow step in eq 4.[6] The presence of the alkyl radical was shown unequivocally by its interception with hexachloroiridate(IV) as described in eq 8 or spin trapping with nitrosoisobutane.[6] Unfortunately, the nature of the cage process inherent in the insertion reaction described in eq 5 precludes the detection of R$\cdot$.[12] There are other reports[2a,13] based on the observation of alkylmetal charge transfer bands, qualitative rate measurements, and ESR studies, which suggest a homolytic cleavage of alkyl-metal bonds by TCNE. However, none of these by themselves present as compelling an example of an electron transfer mechanism as that provided by the studies with organolead compounds.[14]

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(11) The selectivities were determined from the relative amounts of methyl and ethyl adducts to TCNE[3b] as well as the two trialkyllead cations. The latter were obtained by comparison of the 220-MHz ^1H NMR spectra of the trialkyllead chlorides [$Et_3Me_{3-n}PbCl$, $1 \leq n \leq 3$].

(12) Even if some of the ethyl radicals should escape the cage process in reaction 5b, separate experiments show that they add rapidly to TCNE when they are generated independently from the thermal decomposition of dipropionyl peroxide.

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(14) We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance.

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Received April 9, 1975

^2H Spin–Lattice Relaxation in the Presence of Paramagnetic Shift Reagents

Sir:

Spin-lattice relaxation times (T_1) for deuterium are generally more readily interpretable than those for carbon.[1] Experimentally, acquisition of T_1 data for ^2H is less time consuming than for ^{13}C since relaxation times of ^2H are an order of magnitude shorter than those of ^{13}C.[1] These advantages of ^2H over ^{13}C are, however, largely offset by intrinsically low deuterium chemical shifts observed at normal field strengths (scaled down by a factor of 6.5 with respect to their proton counterparts). Thus, in perdeuterated molecules overlapping of resonance signals may effectively preclude determination of relaxation times.

We should like to report that some of the problems associated with the small chemical shift disadvantage of ^2H relative to ^{13}C can be overcome by application of shift reagents. Because of the overwhelming dominance of quadrupolar vs. dipolar relaxation mechanisms in ^2H relaxation,[2] addition of small quantities of paramagnetic shift reagents to readily complexed molecules should produce significant chemical shifts without concomitantly seriously affecting relaxation times. It has been estimated,[2] for example, that the concentration of paramagnetic species large enough to reduce T_1 of ^1H in ^1H_2O by a factor of 400 will shorten T_1 of ^2H in ^2H_2O by a factor of only 2.[3]

To test the feasibility of the utilization of paramagnetic shift reagents in ^2H relaxation time studies, a solution of acetone-d_6 (0.81 *M*) and acetonitrile-d_3 (0.38 *M*) in chloroform was employed. The ^2H NMR spectrum of this mixture exhibited two partially overlapping resonances ($\Delta\nu < 0.1$

ppm at 13.8 MHz) with an intensity ratio of ca. 4:1. The poor resolution vitiated accurate, simultaneous determination of the individual relaxation times. Addition of small quantities of Eu(fod)$_3$ to the extent of $\rho = 0.01$ (ρ being the molar ratio of lanthanide reagent to acetone-d_6) resulted in complete separation of the two resonances ($\Delta\nu = 0.4$ ppm) and allowed simultaneous determination of the individual relaxation times. The relaxation times determined in this manner were found to agree, within experimental error (±10%), with those determined on separate chloroform solutions of the individual components not containing the shift reagent. Subsequent additions of Eu(fod)$_3$ up to and including $\rho = 0.02$ ($\Delta\nu = 0.8$ ppm) led to the same result. *At $\rho > 0.02$ significant shortening of the relaxations times of the components was observed.*

To quantify the effect of Eu(fod)$_3$ on the relaxation time of acetone-d_6 and to probe the nature of the interactions contributing to this effect, the relaxation time of acetone-d_6 in a chloroform solution of acetone-d_6 (0.81 *M*) and CDCl$_3$ (1.0 *M*) (for internal referencing) containing varying amounts of Eu(fod)$_3$, and in separate experiments the diamagnetic La(fod)$_3$,[4] was determined (six samples of each reagent in the range $0.0 \leq \rho \leq 0.14$). At least five separate T_1 measurements were performed on each sample. In this range of ρ the chemical shift of the acetone resonance with respect to internal CDCl$_3$ is linearly correlated with the concentration of Eu(fod)$_3$ (slope of the best least-squares line = 10.2 ppm per unit ρ). Similarly, $1/T_1$ is linearly correlated with respect to ρ. In the case of Eu(fod)$_3$ the slope is 7.03×10^{-1} sec^{-1} per unit ρ (correlation coefficient 0.934) and the intercept ($\rho = 0.0$) is 0.223 sec^{-1}; for La(fod)$_3$ the slope is 6.64×10^{-1} sec^{-1} per unit ρ (correlation coefficient 0.927) and the intercept ($\rho = 0.0$) is 0.223 sec^{-1}.

These findings suggest that the pseudocontact paramagnetic interaction effect (ca. 6%), if experimentally significant, is at best very small in the entire range of ρ studied. Thus, the relaxation of acetone-d_6 in the presence of the lanthanide shift reagent is still primarily dominated by the quadrupolar relaxation mechanism, suggesting that the molecular reorientation time of the acetone molecule is significantly affected by complexation with the bulkier shift reagent molecule. For small ρ (<0.02), however, even this effect is practically negligible. It should be possible, therefore, to employ shift reagents in small quantities for small or strongly complexed molecules, and probably in even greater amounts for large or weakly complexed molecules, to separate overlapping resonances to allow quantitative determination of ^{2}H relaxation times.

Utilization of specifically labeled ^{2}H compounds, in conjunction with shift reagents, should markedly enhance the ability to measure ^{2}H relaxation times; we are currently testing these possibilities on a variety of systems (bicyclics, steroids, acyclics, and aromatics).

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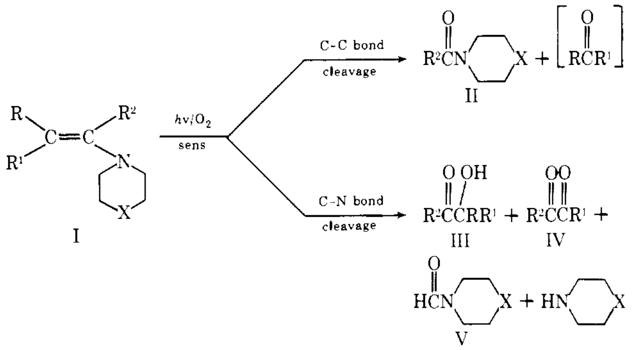
Received May 13, 1975

Singlet Oxygen Reaction. IV. Photooxygenation of Enamines Involving a Two-Step Cleavage of a 1,2-Dioxetane Intermediate[1]

Sir:

Recently, we described the first example of the formation of an α-diketone and an α-hydroxy ketone in the decomposition of 1,2-dioxetane as a possible intermediate in oxygenation of electron rich sulfides.[2,3] The formation of these α-diketones and α-hydroxy ketones was established to involve the two-step biradical cleavage of the intermediate of 1,2-dioxetane. In attempt to find more examples of this two-step biradical process in the decomposition of 1,2-dioxetane intermediate, we examined the photooxygenation of α-alkyl substituted enamine I (R^2 = alkyl), since the relative bond strength of the carbon–nitrogen and carbon–carbon bonds is probably sufficient to make the scission of the carbon-nitrogen bond comparative to that of the carbon–carbon bond.[4] The pioneering work of Foote and Lin have shown that the carbon–carbon double bond of enamine I (R^2 = H) was cleaved to give a ketone or aldehyde and an amide in quantitative yield,[5] and these products appear to originate from decomposition of a 1,2-dioxetane intermediate,[6-9] but by no means requires that the cleavage of 1,2-dioxetane be concerted.[10]

Photooxygenation of Ia in pyridine, at room temperature, sensitized by hemaporphyrin with visible light, proceeded rapidly and ceased abruptly after uptake of approximately 1.2 equiv of oxygen. Both sensitizer and light were found to be essential under the reaction time. Evaporation followed by GLPC gave methyl phenyl diketone (IVa) (30%), 2-hydroxyethyl phenyl ketone (IIIa) (13%), *N*-benzoylmorpholine (IIa) (18%), *N*-formylmorpholine (Va) (10%), and a trace of morpholine; unidentified nonvolatile compounds are also produced.[11] Enamine Ib gave 2-hydroxyisopropyl phenyl ketone (IIIb) (22%), *N*-benzoylmorpholine (IIb) (49%), and a trace of methyl phenyl diketone (IVb). Products were characterized by spectroscopic and gas chromatographic comparison with authentic materials. Addition of 0.1 *M* 2,6-di-*tert*-butylphenol, a good free radical inhibitor, produced no effect either on O$_2$ uptake rate or on product yield in photooxygenation of Ia or Ib. Under the same conditions, enamines Ic, Id, and Ie gave 2-hydroxy ketone, III, and *N*-formyl derivatives V in 10 and 20% yields, respectively, together with the formation of carbon–carbon bond cleavage products II in 20–35% yields.[12] Enamine If gave a trace of 2-hydroxy ketone, III, and produced the carbon–carbon bond cleavage product as a major product (75%).



a, R = H; R^1 = Me; R^2 = Ph; X = O
b, R = R^1 = Me; R^2 = Ph; X = O
c, R = R^1 = Me; R^2 = Ph; X = CH$_2$
d, R = H; R^1 = Me; R^2 = Et; X = O
e, R = H; R^1 = Me; R^2 = Et; X = CH$_2$
f, R = R^1 = Me; R^2 = *i*-Pr; X = O

An overall view of these results summarized in Table I shows that the structural features leading to C–N bond