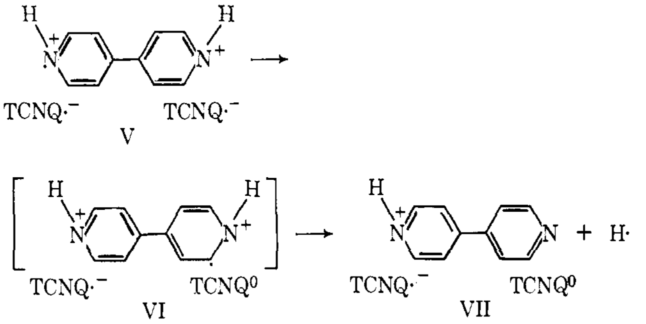
Table III. Correlation of Resistivity with the Ratio TCNQ·$^-$:TCNQ^0

Bipyridylium salt ref no.	Intensity ratio at λ_{max} 3950 Å/λ_{max} 8420 Å	No. of mol in the salt TCNQ·$^-$	TCNQ^0	Resistivity (ρ), ohm cm
4,4′-BP·2HCl	2.25	1	1	1.5
2,2′-BP·2HCl	2.25	1	1	1.4
4,4′-BP·2HI	2.25	1	1	1.2 × 10
4,4′-BP·2CH$_3$I		2	0	1.1 × 10^6
4,4′-BP·2CH$_3$I	1.2	2	1	2.2 × 10

transfer has occurred from TCNQ·$^-$ to the paraquat, where R = H.

The electron transfer results in the oxidation of TCNQ·$^-$ to TCNQ^0 and is therefore responsible for the low resistivity of salts in which the positive nitrogen is bonded to a hydrogen. Thus, the reaction of structure I with 2LiTCNQ·$^-$ leads to a salt containing both the radical anion as well as a neutral TCNQ^0 molecule; therefore, its high electronic conductivity is not surprising. The electron transfer is fairly specific since it does not occur when R = CH$_3$.

In order to account for all the experimental findings the mechanism shown below is proposed. The high electron affinity of I is the driving force for electron transfer which leads to an unstable intermediate, VI. Its presence was not detected spectrophotometrically.[2] It is therefore necessary to postulate an additional step leading to VII with elimination of a hydrogen atom.



V

VI

VII

It is assumed that the hydrogen atom reacts with the solvent or dimerizes and the absence of an electron transfer to methyl-substituted species may be due to the inductive effect of the methyl group which could lower the electron affinity of paraquat salts. Alternatively, a combination of bond strength and solvation energy effects may be operative. The N–CH$_3$ bond being stronger than the N–H bond, the splitting of the hydrogen atom in III could be explained on the basis of bond strength, combined with a higher solvation energy for a hydrogen than for a methyl group. This assumption appears more plausible since the oxidation–reduction potentials of 4,4′-BP·CH$_3$I and 4,4′-BP·HCl determined polarographically, in connection with this investigation, were found to be practically identical, indicating the same electron affinity.

The increase in conductivity of salts containing TCNQ^0 is consistent with the theoretical derivations of LeBlanc[9] who accounted for the high conductivity of the complex salts by hole–electron pairs in the Heitler–London ground-state configuration without placing two electrons on the same TCNQ site and therefore avoiding formation of a dianion. In this interpretation the presence of a neutral TCNQ molecule is necessary for efficient electron transport.

Acknowledgment. This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract No. NAS7-100.

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[9] O. H. LeBlanc, *J. Chem. Phys.*, **42**, 4307 (1965).

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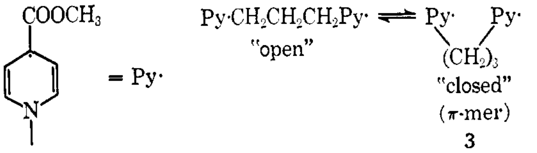
Pyridinyl Diradical π-Mer. Magnesium Iodide Complexes

Sir:

Pyridinyl diradicals associate intramolecularly to form diamagnetic ("closed") complexes,[1] in which the weak delocalized bond between the π systems suggests the generic term π-mer. Formation of π-mers might be expected between (a) pairs of electron-excess systems (ArH·,ArH·), (b) one electron-excess system and a π system (ArH·,ArH), (c) one electron-deficient system and a π system (ArH$^+$,ArH) in those cases for which covalent bond formation is either slow or not especially favorable on energetic grounds. The formation of the intramolecular pyridinyl diradical **3**–π-mer is illustrated in eq 1. We now report a new, remarkable series of intramolecular π-mer–metal halide complexes, which differ in chemical and spectroscopic properties from those of the π-mers in useful and interesting ways.

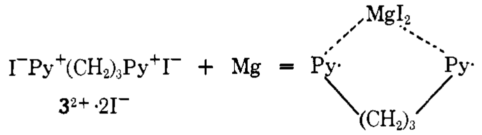


$$\mathrm{Py{\cdot}CH_2CH_2CH_2Py{\cdot}} \rightleftharpoons \underbrace{\mathrm{Py{\cdot}\ \ Py{\cdot}}}_{(\mathrm{CH_2})_3} \qquad (1)$$

"open"

"closed"
(π-mer)
3

Treatment of a thoroughly degassed pale yellow acetonitrile solution of 1,1′-trimethylenebis(4-carbomethyoxypyridinium) diiodide (**3**$^{2+}$·2I$^-$) with excess magnesium turnings at 0° for 10–30 min leads to a royal blue solution of the **3**–MgI$_2$ complex[2] (eq 2). The



$$\mathrm{I^-Py^+(CH_2)_3Py^+I^-} + \mathrm{Mg} = \overset{\mathrm{MgI_2}}{\underbrace{\mathrm{Py{\cdot}\ \ \ Py{\cdot}}}_{(\mathrm{CH_2})_3}} \qquad (2)$$

3^{2+}·2I$^-$

3–MgI$_2$

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[1] M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 1843 (1968).

[2] Initial work on monopyridinyl radicals[3] indicated clearly that metal halides (magnesium, zinc iodides) complexed with 1-alkyl-4-carbomethoxypyridinyls.

[3] E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964).

spectrum of the complex differs from that of the diradical **3** in several striking ways: (a) the longest wavelength band is tripled in intensity and shifted 1000 Å to shorter wavelengths, (b) the first ultraviolet absorption band is narrowed and shifted somewhat to shorter wavelengths, (c) the second ultraviolet absorption band appears as a narrow intense band in place of a broad low band. A simple molecular orbital treatment permits a tentative assignment of the transitions in the MgI_2 complex, and therefore of diradical **3**. The spectra of **3** and **3**–MgI_2 are shown in Figure 1. The assignment will be discussed in detail in a full paper.

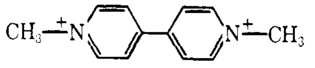
Titration of the **3**–MgI_2 complex with excess methylviologen dichloride (MD^{2+}) indicates that the complex has two more electrons than the precursor diiodide. The magnesium content of the solution corresponds to one atom of magnesium for each mole of diiodide, and oxidation with oxygen produces 1 mol of hydrogen peroxide and 1 mol of 1,1′-trimethylenebispyridinium ion for each mole of diiodide (3^{2+}) originally reduced.

The diradical **3**–MgI_2 complex exhibits a weaker epr signal than the diradical **3** itself. The stronger and sharper light absorption spectrum together with the weaker epr signal from solutions of the **3**–MgI_2 complex suggest that the magnesium ion is coordinated to the ester groups of both pyridinyl radicals, serving to orient them and to hold them together. Thus, as expected, the magnesium iodide complex of the pentamethylene diradical (**5**–MgI_2) behaves as a π-mer, although the diradical **5** itself shows no intramolecular complex formation.[1]

The **3**–MgI_2 complex is far more reactive chemically than the diradical **3** or the corresponding monoradical. Qualitatively, **3**–MgI_2 reacts much faster with methylviologen (MD^{2+}) than **3** itself. Quantitatively, the rate of reaction of **3**–MgI_2 with methyl iodide is about 100 times faster than that of the 1-ethyl-4-carbomethoxypyridinyl[4] and almost 10^4 faster than the reaction of diradical **3** with methyl iodide.

The calcium, zinc, and manganese complexes, **3**–CaI_2, **3**–ZnI_2, and **3**–MnI_2, can be prepared from the diiodide and the metals in acetonitrile. The spectrum of the calcium complex is slightly different from that of the magnesium complex; the spectra of the other complexes differ more substantially from that of the magnesium complex.

Preliminary examination of the series in which the number of methylene groups between the pyridinyl radical moieties is varied from 3 to 10 indicates that intramolecular π-mer formation can be induced by magnesium iodide for a diradical containing as many as six methylene groups.



MD^{2+}

The discovery of these radical–metal ion complexes presents many new and exciting opportunities for chemical, epr, and spectroscopic studies, and clearly offers new possibilities for introducing and controlling π-mer interactions, in simple as well as polymeric systems.

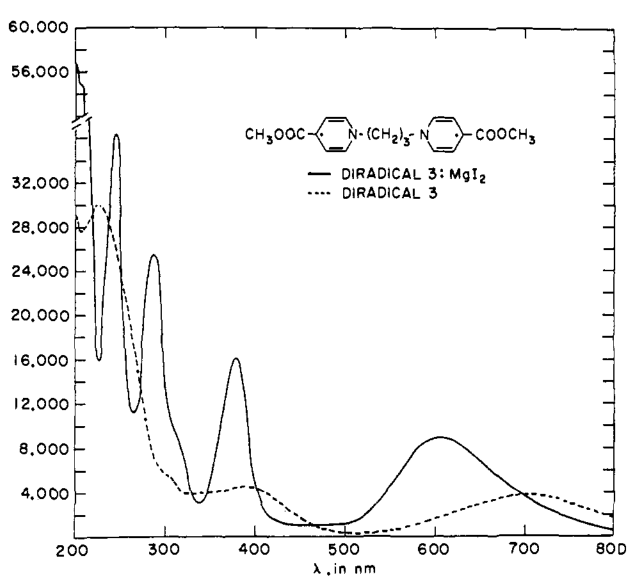


Figure 1. The spectra of diradical **3** and the **3**-MgI_2 complex in acetonitrile at 25°. The previously reported spectrum of **3**[1] is the same as that shown here but terminated at about 300 nm.

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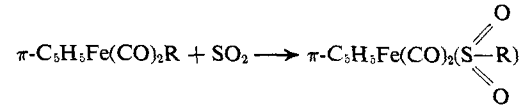
[4] E. M. Kosower and I. Schwager, *J. Amer. Chem. Soc.*, **86**, 5528 (1964).

Electronic Effects in Sulfur Dioxide Insertion Reactions[1]

Sir:

Although sulfur dioxide insertion reactions of metal alkyl complexes have been studied extensively under synthetic conditions,[2] kinetic data on these processes are still lacking. Neither have there been any attempts at a systematic investigation of the dependence of metal alkyl reactivity on electronic and structural factors. To fill the existing void and to complement our preparative efforts we have now initiated a kinetic study on these reactions. Inasmuch as our early findings are very relevant to the rapidly developing concept of transition metal basicity,[3] and in view of the widespread interest in insertion reactions and related processes,[4] we herein report some preliminary results.

The reaction[5]



$$\pi\text{-}C_5H_5Fe(CO)_2R + SO_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2(S(=O)_2\text{—}R)$$

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[1] Sulfur Dioxide Insertion. XIV. For part XIII of this series, see D. A. Ross and A. Wojcicki, *Inorg. Chim. Acta*, in press.

[2] M. Graziani and A. Wojcicki, *ibid.*, 4, 347 (1970), and references therein.

[3] See, for example, D. F. Shriver, *Accounts Chem. Res.*, 3, 231 (1970).

[4] See, *inter alios*, M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, 5, 225 (1967); J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

[5] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966).