The F values (fraction of ion pairs going to product) for **1a** and **1b** are calculated to be 1.0 and 0.81, respectively, in buffered acetolysis after one $t_{1/2}$ assuming no secondary α-deuterium isotope effect in the reaction of **4b** with solvent.[18] Since the reactivities of **1b** and **2** are nearly the same (Table I), a similarity in their F values would be expected; Coke[2d] has assigned $F = 0.466 \pm 0.017$ for acetolysis of **2**. This apparent inconsistency is due to a special salt effect by KOAc for **2**[18–21] which is also believed operating in the buffered acetolysis of **1b**. We believe that this is apparent when the titrimetric and conductometric data for **1a**, **1b**, and **2** (Table I) are compared.[22]

From the deuterium scrambling data for **1b** (Table II), the acetate product shows about 2 ± 1% of the k_s pathway present. On the basis of 2% k_s, we calculate $k_s = 2 \times 10^{-6}$ sec^{-1} (90°) under these conditions in good agreement with the value of Coke, $k_s = (3.5 \pm 3.1) \times 10^{-6}$ sec^{-1}, for **2** at 90°.[2d] Since k_s has been shown to change little as a function of aryl ring substituent,[2a,b] we conclude that **1a** and **1c**–**1e** undergo buffered acetolysis totally by the k_Δ pathway.

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(19) J. R. Curtis, Ph.D. Thesis, Kansas State University, 1971.

(20) S. Winstein, P. E. Klinedinst, and G. C. Robinson (*J. Amer. Chem. Soc.*, **83**, 885 (1961)) reported special salt effects for tetrabutylammonium acetate and lithium acetate in the acetolysis of 1-anisyl-2-propyl OTs and 3-anisyl-2-butyl OBs, respectively.

(21) Buffered acetolysis of **2**-*1,1-d*$_2$ (0.010 *M* ROTs, 0.012 *M* KOAc) at 95.0° shows 8 ± 1% label scramble in recovered tosylate and 0 ± 1% of the k_s pathway after 50% reaction with $F \approx 0.76$. Unbuffered acetolysis of **2**-*1,1-d*$_2$ showed 35 ± 1% label scramble in recovered tosylate after 46% reaction at 75.0° ($F \approx 0.40$) and 35 ± 1% label scramble after 50% reaction at 95.0°. E. F. Jenny and S. Winstein (*Helv. Chim. Acta*, **41**, 807 (1958)) reported that unbuffered acetolysis of 2-*1*-^{14}C (0.050 *M* ROTs) gave 38% label scramble after 38% reaction ($F = 0.33$) which was reduced to 5% after 49% reaction ($F = 0.83$) by addition of 0.010 *M* $LiClO_4$ at 75.0°. The disagreement in the scrambling data from the two methods at 75° in the absence of added salt is not understood.

(22) For **1a** we see the same rate in going from 0.010 *M* ROTs and 0.012 *M* KOAc (titrimetric) to 0.0010 *M* ROTs and 0.0012 *M* KOAc (conductometric). The same concentration change with **1b** leads to a 6–7% reduction in the rate constant while a smaller concentration change with **2** (0.005 *M* ROTs and 0.006 *M* KOAc for titrimetric data) is found to give a larger, 19 ± 4%, rate reduction.[23] This should be reflected in the F values for **1b** and **2** in unbuffered acetolysis, the F for **1b** being larger than that of **2**. The present data allow only the observation that such appears to be the case.

(23) Generally, agreement in rate constants determined by these two methods has been excellent with the conductometric[6b] k_t about 1% larger than the titrimetric[6a] k_t in the absence of special effects;[24] R. N. McDonald and G. E. Davis, unpublished results.

(24) B. L. Murr and V. J. Shiner (*J. Amer. Chem. Soc.*, **84**, 4672 (1962)) have arrived at a similar conclusion.

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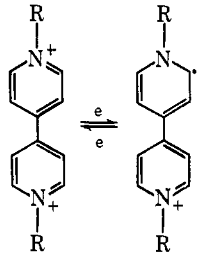
Electron Transfer to Bipyridilium (Paraquat) Salts

Sir:

The high electron affinity of 4,4′-bipyridilium (paraquat) salts, well-known herbicides,[1] has been demonstrated already in 1933 by Michaelis and Hill[2] who have shown that bipyridilium bases can be reduced to form colored species. The colorless bivalent cation accepts an electron to form II, a violet univalent cation, and this process may be represented by the following equilibrium

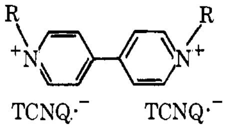


I II

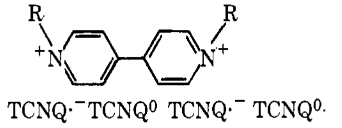
where R is generally an aryl or alkyl group or a hydrogen atom and the counterion is omitted.

The ease of reduction of paraquat is attributed to its high electron affinity which is also responsible for the formation of a variety of charge-transfer complexes between paraquats and phenols, quinones, hydroquinones, etc.,[3–5] the latter acting as electron donors and the paraquats as electron acceptors.

Bipyridils also form two types of electrically conducting salts when treated under suitable conditions with 7,7,8,8-tetracyanoquinodimethane (TCNQ) or its derivatives. These can be represented by structures III and IV where TCNQ·⁻ denotes the radical anion



III



IV

and TCNQ^0 the neutral molecule. The TCNQ salts of mono- or polyammonium salts differ from charge-transfer complexes since in the latter an equilibrium is established between the donor, acceptor, and the complex, while in TCNQ salts, an unpaired electron is believed to be delocalized over the domains of TCNQ rings leading to a relatively high electrical conductivity. Structure III is formed by the reaction of two LiTCNQ·⁻ molecules with one molecule of I and its specific resistivity is several orders of magnitude higher than the resistivity of structure IV which is formed when two neutral TCNQ molecules are added to III. The dramatic decrease in resistivity is attributed to the enhanced electron transport in the presence of neutral TCNQ and these facts are in agreement with previous results pertaining to a large number of TCNQ salts and their anisotropic conductivity which is highest in the direction perpendicular to the TCNQ rings.[6,7]

(1) W. R. Boon, *Endeavour*, **26**, 27 (1967).

(2) L. Michaelis and E. S. Hill, *J. Gen. Phys.*, **16**, 859 (1933).

(3) A. J. MacFarlane and R. T. P. Williams, *J. Chem. Soc. A*, 1517 (1969).

(4) B. G. White, *Trans. Faraday Soc.*, **65**, 2000 (1969).

(5) A. Ledwith and H. J. Woods, *J. Chem. Soc.*, 1422 (1970).

(6) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

Table I. Aliphatic Diammonium TCNQ Salts

Diammonium salt	Ratio used in synthesis 1 M diam salt : 2 M $Li^+TCNQ\cdot^-$			Ratio used in synthesis 1 M diam salt : 2 M $Li^+TCNQ\cdot^-$: 2 M $TCNQ^0$		
	Resistivity (ρ), ohm × cm	Activation energy (ϵ), eV	Seebeck coeff (α), $\mu V/°C$	Resistivity (ρ), ohm × cm	Activation energy (ϵ), eV	Seebeck coeff (α), $\mu V/°C$
$(CH_3)_3N^+(CH_2)_5N^+(CH_3)_3 \cdot 2Br^-$	4.0×10^6	0.29	+410	1.2×10^2	0.22	−150
$(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3 \cdot 2I^-$	5.0×10^{10}	0.73		1.0×10^2	0.21	−143
$(CH_3)_3N^+(CH_2)_8N^+(CH_3)_3 \cdot 2Br^-$	3.7×10^7	0.41	+720	7.0	0.090	−10

Table II. Bipyridylium TCNQ Salts

Bipyridylium salt	Ratio used in synthesis 1 M BP salt : 2 M $Li^+TCNQ\cdot$			Ratio used in synthesis 1 M BP salt : 2 M $Li^+TCNQ\cdot^-$: 2 M $TCNQ^0$		
	Resistivity, ohm cm	Activation energy (ϵ), eV	Seebeck coeff (α), $\mu V/°C$	Resistivity (ρ), ohm cm	Activation energy (ϵ), eV	Seebeck coeff (α), $\mu V/°C$
4,4′-BP·2HCl	1.5	0.090	−66	1.2	0.098	−65
2,2′-BP·2HCl	1.4	0.060	−56	1.0	0.058	−52
4,4′-BP·2HI	12.0	0.110	−65	9.0	0.103	−66
4,4′-BP·$2CH_3I$	1.1×10^6	0.65	+150	22.0	0.130	−37

In this communication we report an exceptionally low specific resistivity of paraquats, in which R = H, formed without the addition of neutral TCNQ. We attribute this phenomenon to an electron transfer from $TCNQ\cdot^-$ to the bipyridil moiety which is probably followed by a molecular rearrangement. Our findings may be summarized as follows. (1) The paraquat salt I in which R = H, when allowed to react with two molecules of $LiTCNQ\cdot^-$, exhibits an electrical resistivity of about 1–10 ohm cm and on addition of neutral TCNQ the electrical resistivity remains unaltered. Furthermore, the same salt with R = CH_3 formed under identical conditions is characterized by a resistivity of the order of 10^6 ohm cm. However, the addition of neutral TCNQ to the latter reduces the electrical resistivity by about five orders of magnitude. (2) The visible spectra of the aliphatic diammonium and bipyridilium TCNQ salts (structure III) exhibited the characteristic features previously reported for a number of other TCNQ compounds.[6,7] Bipyridil quaternized with HCl or HI and reacted with $2LiTCNQ\cdot^-$ is an exception. In this case the absorption bands of neutral $TCNQ^0$ are clearly distinguishable in the reaction product. (3) The absorption spectrum of paraquat (structure I or II) with different anions does not overlap with the absorption spectra of TCNQ salts.[2,6,7] (4) The electronic transport properties of aliphatic diammonium TCNQ salts do not differ significantly from the corresponding bipyridilium salts, with the exception of the case where electron transfer occurs (when R = H). (5) The exceptionally low resistivity of paraquats formed by addition of $2LiTCNQ\cdot^-$ may be explained by an electron-transfer reaction which leaves $TCNQ^0$ in the resulting structure (see VII).

The investigated samples were prepared by treating 1 mol of the diammonium salt in the form of dichloride or diodide with 2 mol of $LiTCNQ\cdot^-$ or with 2 mol of $LiTCNQ\cdot^-$ and 2 mol of $TCNQ^0$.

The specific electrical resistivity was determined by a previously described technique[7] and verified by means of an instrument recently reported.[8] The amounts of $TCNQ\cdot^-$ and $TCNQ^0$ in the various salts could be determined spectrophotometrically by means of a calibration curve using synthetic mixtures of $LiTCNQ\cdot^-$ and $TCNQ^0$ shown in Figure 1.

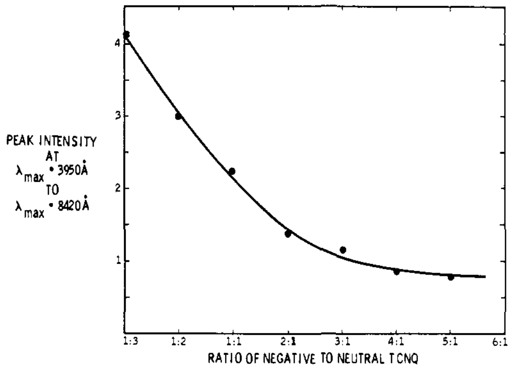


Figure 1.

In Tables I and II are shown the electronic transport properties of aliphatic diammonium compounds and bipyridilium TCNQ salts, respectively.

Table I confirms the previous results,[7] namely, the electrical resistivity of diammonium TCNQ salts, in which both positive nitrogens are associated with a $TCNQ\cdot^-$, is five–six orders of magnitude higher than the resistivity of the same compounds containing, in addition to the radical ion ($TCNQ\cdot^-$), a neutral TCNQ molecule.

Table II illustrates the same facts for *N,N′*-dimethyl-4,4′-bipyridilium TCNQ compound (4,4′-BP$2CH_3I$). However, the *N,N′*-dihydro-4,4′- and -2,2′-bipyridilium TCNQ salts (4,4′-BP·2HCl and 2,2′-BP·2HCl) constitute exceptions of what appeared to be a general rule.

Table III shows that the paraquat TCNQ salts exhibiting the anomalous low resistivity contain $TCNQ^0$.

On the basis of the results shown in Tables I, II, and III, it is possible to conclude that an electron

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[7] A. Rembaum, A. M. Hermann, F. E. Stewart, and F. Gutmann, *J. Phys. Chem.*, 73, 513 (1969).

[8] V. Hadek, *Rev. Sci. Instrum.*, 42, 393 (1971).

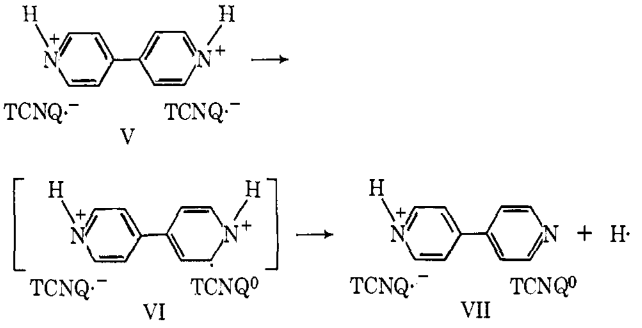
Table III. Correlation of Resistivity with the Ratio $TCNQ\cdot^-$:$TCNQ^0$

Bipyridylium salt ref no.	Intensity ratio at λ_{max} 3950 Å/λ_{max} 8420 Å	No. of mol in the salt $TCNQ\cdot^-$	$TCNQ^0$	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_3I		2	0	1.1×10^6
4,4′-BP·2CH_3I	1.2	2	1	2.2×10

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

The electron transfer results in the oxidation of $TCNQ\cdot^-$ 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 2Li$TCNQ\cdot^-$ 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_3I 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).

[10] NRC-NASA Resident Research Associate.

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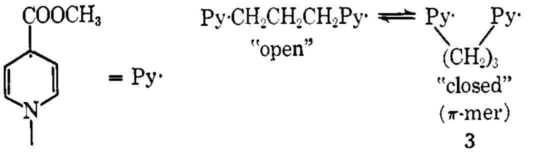
Pyridinyl Diradical π-Mer. Magnesium Iodide Complexes

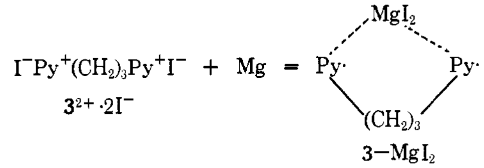
Sir:

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.



(1)

Treatment of a thoroughly degassed pale yellow acetonitrile solution of 1,1′-trimethylenebis(4-carbomethyoxypyridinium) diiodide ($3^{2+}\cdot 2I^-$) 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



(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).