

being made in an effort to better understand the geometries and bonding in these compounds.

(12) NASA Trainee, 1966-1968.

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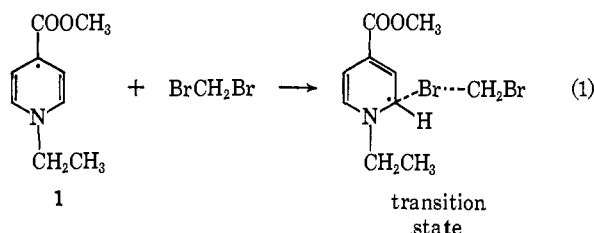
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The Solvent Effect on an Electron-Transfer Reaction of Pyridinyl Radicals

Sir:

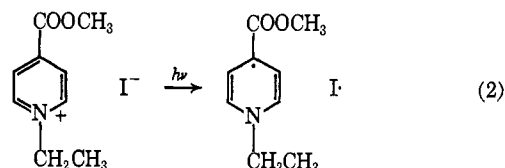
Pyridinyl radicals react with halocarbons at rates which are very sensitive to the structure of the halocarbon.¹ Rate constants for the reaction of 1-ethyl-4-carbomethoxy-pyridinyl (1) with tetrachloromethane and dichloromethane differ by a factor of 10^8 . The negligible effect of solvent polarity on the rate of reaction of 1 with dibromomethane implies an atom-transfer mechanism (eq 1). Most *para*-substituted benzyl



chlorides appear to react with the pyridinyl radical 1 by the atom-transfer route judging from the rather small substituent effects observed (4-OCH₃, 4-CH₃, H, 4-Cl derivatives exhibit rate constants which differ by a

an enormous solvent effect on the rate of the reaction.

Not only is the solvent effect on the reaction of 1 with 4-nitrobenzyl chloride large, but the change in rate constant for the change in solvent from 2-methyltetrahydrofuran to acetonitrile is on the order of that expected for a reaction in which an ion pair is created from a pair of neutral molecules. The fundamental process to which we can refer is that for the solvent polarity standard, *Z* value (the destruction of an ion pair through charge transfer, eq 2).² The operation



of the Franck-Condon principle (electronic motion much faster than nuclear motion) brings about an excited state from the charge-transfer transition which is destabilized to the same extent that the ground state is stabilized. We would thus predict that creation of an ion pair in a thermal process should have a solvent sensitivity of about $0.5\Delta Z$. Data illustrating this point are given in Table I.

There seems to be only one previous report of a large solvent effect on the rate of a reaction in which electron transfer may be involved. In that case, the reaction of 4-methoxystyrene with tetracyanoethylene to form a cyclobutane has a rate which is very sensitive to solvent.³

A portion of the mechanism of the reaction of the pyridinyl radical 1 with 4-nitrobenzyl chloride is shown in eq 3.

Table I. Rates of Reaction of 1-Ethyl-4-carbomethoxy-pyridinyl (1)^a with Benzyl Chlorides^{b,c}

Benzyl chloride ^d (C ₀) ^e	Solvent (Z) ^f	Radical 1 (C ₀) ^e	k ₂ , l. mol ⁻¹ sec ⁻¹ ^g
4-CH ₃ O (∞0.4)	CH ₃ CN	(∞0.02)	1.13 × 10 ⁻³
4-CH ₃ (∞0.6)	CH ₃ CN	(∞0.025)	3.68 × 10 ⁻⁴
4-H (∞1.0)	CH ₃ CN	(∞0.008)	3.31 × 10 ⁻⁴
4-Cl (∞0.4)	CH ₃ CN	(∞0.01)	6.5 × 10 ⁻⁴
4-NO ₂ (∞10 ⁻⁵)	CH ₃ CN (71.3)	(∞10 ⁻⁵)	2.4 × 10 ⁴
(∞10 ⁻⁵)	DMF ^h (68.4)	(∞10 ⁻⁵)	1.2 × 10 ⁴
(∞10 ⁻⁵)	CH ₃ COCH ₃ (65.5)	(∞10 ⁻⁵)	450
(∞10 ⁻⁴)	CH ₂ Cl ₂ (64.7)	(∞10 ⁻⁴)	~75
(∞10 ⁻⁴)	DME ⁱ (59.1)	(∞10 ⁻⁵)	8.3
(10 ⁻⁵ -10 ⁻⁴)	MTHF ^j (55.3)	(∞10 ⁻⁵)	1.62

^a Radical was prepared by the procedure previously reported (ref 1 and E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964)) as modified by H. P. Waits and E. M. Kosower, 148th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, S109. ^b Rates were followed spectrophotometrically in all-glass apparatus. The procedure differed from that outlined in ref 1 in that no stopcocks were used which could come into contact with the radical solution, the halide solution, and/or liquid solvent. Furthermore, the major part of the apparatus was rinsed with free-radical solution before mixing with the halide in all cases in which dilute radical solutions were used (dilute = 10⁻³ M or less). ^c All rate constants were measured at 25°. ^d All benzyl chlorides and solvents were subjected to rigorous purification and analysis. Details will be presented in a full publication. ^e Approximate range of concentration used in kinetic runs in moles/liter. ^f All *Z* values were new determinations, made with 1-ethyl-4-carbomethoxy-pyridinium iodide² and extrapolated to infinite dilution. ^g All rate constants are the average of two determinations, except for those for MTHF (four runs), DMF (one run), and 4-chlorobenzyl chloride (one run). Reproducibility was ±10% or better in most cases. ^h Dimethylformamide. ⁱ 1,2-Dimethoxyethane. ^j 2-Methyltetrahydrofuran.

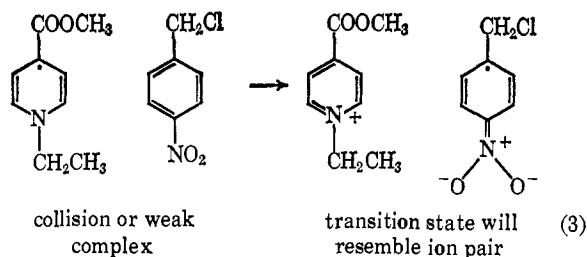
factor of less than 4) (Table I). We have now found that 4-nitrobenzyl chloride reacts with 1 in acetonitrile much faster than other benzyl chlorides. The rate factor is so large that a change in mechanism must be involved, and we have confirmed that an electron-transfer process is involved by the demonstration of

A number of interesting reactions involving 4-nitrobenzyl chloride as an electron acceptor have been reported by Kornblum and coworkers.⁴

(2) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968.

(3) D. A. Wiley and H. E. Simmons, cited by E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 124 (1965); D. W. Wiley, to be published. We thank Dr. Wiley for a preprint of his paper.

(1) E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5528 (1964).



We have established that solvent effects are strong criteria in reaching decisions about the mechanisms of radical reactions. For systems in which specific solvation is not dominant (as it is in oxy radicals), a small solvent effect implies an atom-transfer reaction and a large solvent effect suggests an electron-transfer reaction. The high solvent sensitivity of electron-transfer reactions should provide a useful test for their occurrence.

Acknowledgment. The authors are grateful to the Research Laboratories, Edgewood, Md., for support through Contract DA 18-035-AMC-138(A).

(4) N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, **88**, 5660, 5662 (1966); **87**, 4520 (1965).

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Organometallic Sulfur Complexes. XIII. Synthesis, Structure, and Bonding of a New Metal-Sulfur Cluster System, $S_2Ni_3(C_5H_5)_3$. The Influence of Valence Electrons on Molecular Geometry¹

Sir:

In the course of our systematic structural investigations of organometallic chalcogen complexes, the synthesis of $SNi_3(C_5H_5)_3$, an electronic equivalent of the previously reported $SCo_3(CO)_9$,^{2,3} was attempted. The reaction in organic solvents of $[C_5H_5NiCO]_2$ with sulfur in varying ratios led, however, to the formation in low yield of the new paramagnetic compound tris(cyclopentadienylnickel) disulfide, $S_2Ni_3(C_5H_5)_3$. The constitution of $S_2Ni_3(C_5H_5)_3$ was determined by full elemental analysis, infrared spectrum, and magnetic measurement which gave a μ_{eff} of 1.7 BM corresponding to one unpaired electron.

$S_2Ni_3(C_5H_5)_3$ crystallizes in the hexagonal system with $a = 9.595 \pm 0.006$ Å, $c = 9.923 \pm 0.006$ Å; $\rho_{obsd} = 1.89$ (floatation method) *vs.* 1.83 g cm⁻³ based on two formula species per cell. All crystals examined by X-ray photographs invariably showed $D_{6h} \cdot 6/m2/m2/m$ Laue symmetry. Systematic absences of l odd for $\{000\}$ indicate a 6₃ axis in the c direction. Three-dimensional intensity data were collected with Mo K α radiation on a General Electric four-angle automatic diffractometer. Attempts to interpret a computed three-dimensional Patterson function on the basis of the apparent space group $P6_322$ ($D_{6h} \cdot 6$, No. 182),⁴

(1) Previous paper in this series: C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, in press.

(2) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

(3) S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometal. Chem.* (Amsterdam), **1**, 373 (1964), and references therein.

(4) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

uniquely defined by the above symmetry requirements, were unsuccessful. Instead this interatomic vector map can be explained only in terms of an incoherent twinning mechanism involving an individual hexagonal single-crystal component of symmetry $P6_3/m$ (C_{6h}^2 , No. 176).⁴ The twinning of the reciprocal lattice of this individual crystal of $C_{6h} \cdot 6/m$ point group symmetry by an operation such as reflection across a (100) mirror plane would give rise to a twin composite with the same apparent hexagonal unit cell but of the observed D_{6h} symmetry. The determination of the cyclopentadienyl rings in this twinned crystal by Fourier syntheses was done by the Wei procedure⁵ which enabled a breakdown of the observed $F(hkl)^2$ data for the twin composite into the appropriate $F(hkl)$ coefficients for the single-crystal component. The incoherent twinning model was verified by a successful full-matrix, least-squares rigid-body refinement⁶ which yielded an $R_1(F^2)$ of 10.2%. In this refinement the cyclopentadienyl parameters were constrained to a regular pentagonal ring geometry; anisotropic thermal parameters were utilized for the nickel atom and isotropic ones for the sulfur and individual carbon atoms.

Crystalline $S_2Ni_3(C_5H_5)_3$ consists of discrete molecules with the configuration shown in Figure 1. The nickel and sulfur atoms form a regular trigonal bipyramid with the cyclopentadienyl rings stereochemically disposed about the nickel atoms such that lines passing from the center of the equilateral nickel triangle through the nickel atoms intersect the centroids of the cyclopentadienyl rings. With the assumption of cylindrical symmetry for each cyclopentadienyl ring, the molecular configuration of $S_2Ni_3(C_5H_5)_3$ approximately possesses $D_{3h} \cdot 62m$ symmetry; the local crystallographically demanded site symmetry for each molecule based on a twofold orientational disorder of each cyclopentadienyl ring is $C_{3h} \cdot \bar{6}$. The important bond lengths (with individual esd's of the last significant figures given in parentheses) are Ni-Ni = 2.801 (5) Å, Ni-S = 2.172 (6) Å, Ni-C (av) = 2.13 Å; the Ni-S-Ni and S-Ni-S angles are 80.3 (3) and 83.8° (4), respectively. This unusually long Ni-Ni distance is approximately 0.4 Å greater than that observed in other polynuclear organometallic complexes containing nickel triangles,^{7,8} whereas the Ni-S bond length is in the range normally observed for triply bridging substituent-free sulfur atoms.^{1,2,9} Both the relatively small intramolecular S...S distance of 2.90 (2) Å and the rather acute S-Ni-S angle can be attributed to a compression of the trigonal bipyramidal S_2Ni_3 fragment due to the long Ni-Ni distances.

A consideration of bonding schemes to rationalize these molecular features is informative. As in other

(5) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967); C. H. Wei, Abstracts of Papers, National Meeting of the American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 20-25, 1967, p 83.

(6) The function minimized was $\sum w[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2$, where s is the one adjusted scale factor; $R_1(F^2) = \{[\sum ||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|] / \sum |F(hkl)_o|^2\} \times 100$.

(7) A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 640.

(8) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968).

(9) D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3727 (1967); C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966); R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966).