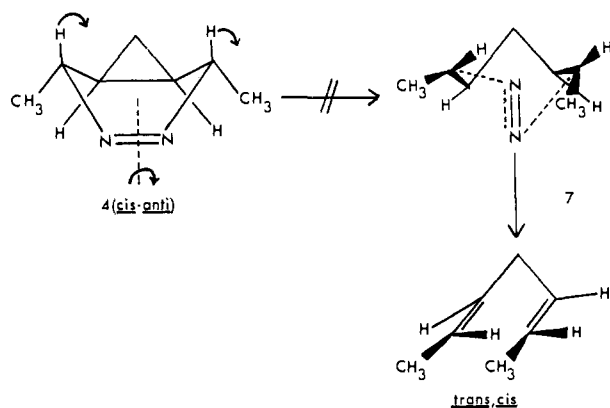


which incidentally fails to show any evidence of CIDNP signals⁷ (under the admittedly narrow range of conditions so far examined). The products (>99.5% stereospecific) are the previously reported⁴ 2,5-heptadienes: *trans,trans* from **4**, *trans,cis* from **5**, and *cis,cis* from **6**.

The course of irradiation of the azo compounds at -70° with a Pyrex-filtered 450-W Hanovia mercury lamp is followed spectrophotometrically (solution temperature monitored with internal thermocouple). After disappearance of the azo chromophore, the diene product is isolated with >99.5% stereospecificity. Again, the results are **4** \rightarrow *trans,trans*, **5** \rightarrow *trans,cis*, and **6** \rightarrow *cis,cis*.

One strong *extrasymmetric*⁸ factor that probably is at



work in both the thermal and photochemical reactions is that which opposes the *trans* expulsion of nitrogen. This path has a large twisting component (*cf.* **4** \rightarrow **7**) and results in *conrotation* of the methyl-bearing carbons, an odd-s process thermally "allowed" by the simple orbital symmetry rules. Presumably, this does not occur in the thermal reaction because it requires substantial disruption of the nonreacting azo N-N π bond. It may be that, in the excited state, this extrasymmetric prohibition is overcome (for example, by *cis* \rightarrow *trans* isomerization of the azo link in the π, π^* state). The photochemically "allowed" even-s paths from electronically excited *trans*-azo compound then would lead by *disrotation* to just those products observed. The same products would result from internal conversion of an electronically excited state to a vibrationally excited *cis*-azo ground state followed by odd-s "thermal" reaction of the latter.

Detailed correlation diagrams, which will appear in a full paper, suggest that the observations may have a more complex origin. For the present, we note that the results of such diagrams depend upon the ordering of the energy levels and upon whether the photodecomposition occurs in the n, π^* or π, π^* state. Moreover, the diagrams imply two speculative but intriguing possibilities. If reaction is from n, π^* , it may be facilitated by a symmetry-allowed crossing to ground state along the reaction coordinate.⁹ If reaction is from π, π^* triplet (perhaps formed by internal conversion from

(7) *Cf.* H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and references cited there.

(8) We suggest this term as a general one for those influences other than orbital sign relationships (*e.g.*, minimum distortion, orbital overlap, steric strain, proximity of reactive sites, etc.) which play a role in determining the course of reaction.

(9) For a similar crossing postulated on a more quantitative theoretical basis, see W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Am. Chem. Soc.*, **91**, 6042 (1969).

n, π^* singlet¹⁰), a crude energy calculation suggests that even though photochemical promotion of azo compound to its $^1(n, \pi^*)$ state provides only about 3.2 eV of excess energy, the exothermicity of the decomposition may suffice to permit formation of the lowest triplet of nitrogen, which is 6.16 eV above ground.^{11,12} The second possibility is subject to experimental test.

Although a choice among these and other possible explanations¹³ must await a more complete study, the present results already illustrate the inadequacy of predictions based solely upon the symmetry properties of the reacting bond orbitals (*i.e.*, simple orbital symmetry rules). They emphasize the need for caution in the theoretical analysis of concerted reactions involving heteroatoms.

(10) (a) *Cf.* I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969). (b) Acetophenone sensitizes the photolysis of **4**, and piperylene (1.0 M) does not quench the direct photodecomposition of **5**. The product dienes are again *trans,trans* and *trans,cis*, respectively.

(11) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, p 449.

(12) *Cf.* A. Ganzow, M. Z. Hoffman, N. N. Lichtin, and S. K. Wason, *J. Phys. Chem.*, **72**, 3749 (1968).

(13) (a) For example, the corresponding diazenes^{13b} might be photo-intermediates. More detailed correlation diagrams now indicate that these could give the observed products in thermally or photochemically allowed processes. (b) D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

(14) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowship No. 2FO2CA25233-02 from the National Cancer Institute.

Jerome A. Berson, Stephen S. Olin¹⁴

Departments of Chemistry
Yale University, New Haven, Connecticut 06520
University of Wisconsin, Madison Wisconsin 53706

Received October 27, 1969

π -Cyclobutadieneiron Ions in the Mass Spectrometer. Evidence by Labeling

Sir:

The mass spectra of C_4 compounds must be reconciled with carbon-skeleton scrambling which is nearly complete in many instances; for example, ^{13}C -labeled butene ions show a statistical loss of methyl containing each carbon atom of the chain when the $C_3H_5^+$ is produced, an observation which can be reconciled by an insertion mechanism whose rate is at least competitive with fragmentation.¹ Similarly, scrambling studies of phenylated compounds producing $C_4Ar_4^+$ have in the past always shown almost complete scrambling before this ion halves to give $C_2Ar_2^+$.² The latter data are consistent with the production of a tetrahedral symmetry in $C_4Ar_4^+$ before it fragments, but not with mechanisms where scrambling in the molecular ion itself occurs;³ again, the results may be explained by some sort of insertion mechanism which produces nearly statistical scrambling before fragmentation.

Our interest in the structures of ligands originally π bonded to transition metals in organometallic mass spectra^{4,5} suggested experiments to determine whether

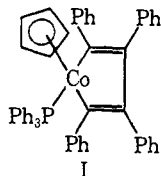
(1) G. G. Meisels, J. Y. Park, and B. G. Giesser, *J. Amer. Chem. Soc.*, **91**, 1555 (1969).

(2) M. M. Bursey and T. A. Elwood, *ibid.*, **91**, 3812 (1969), and references contained therein.

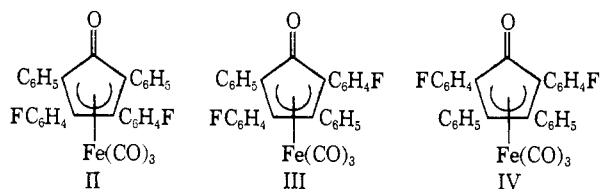
(3) M. K. Hoffman, *et al.*, submitted for publication.

(4) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **90**, 973 (1968), and references contained therein.

the presence of a π -bonded transition metal atom would alter the scrambling pattern observed in the purely organic systems studied so far. We anticipated that a tricarbonyliron complex might exert an effect in gaseous ions similar to the stabilization of cyclobutadiene by iron⁶ or the formation of a metallocycle like the cobalt derivative I suggested by Hagihara.⁷



We report now that for the first time scrambling results have been obtained supporting the formation of cyclobutadiene structures, in the tetracyclone complexes II, III, and IV prepared by irradiation of solutions of the corresponding tetracyclones^{8,9} and $\text{Fe}(\text{CO})_5$ according to the method of Schrauzer.¹⁰ The spectra of these complexes were found to be generally similar to that of π -tetracyclonetricarbonylruthenium.¹¹ In particular, we observed decompositions to $\text{C}_2\text{Ar}_2\text{Fe}^+$ from $\text{C}_4\text{Ar}_4\text{COFe}^+$ (*i.e.*, $[\text{M} - 3\text{CO}]^+$) and $\text{C}_4\text{Ar}_4\text{Fe}^+$ (*i.e.*, $[\text{M} - 4\text{CO}]^+$) supported by relatively intense metastable peaks. The $[\text{M} - 4\text{CO}]^+$ peak itself is weak in these spectra, as it is in the Ru spectrum, but the metastable decompositions relating it to various $\text{C}_2\text{Ar}_2\text{Fe}^+$ ions produce measurable metastable peaks.¹²



Data for the metastable decompositions of the m/e ion $[\text{C}_4(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{F})_2\text{Fe}^+]$ to m/e 234 $[(\text{C}_6\text{H}_5)_2\text{C}_2\text{Fe}^+]$, 252 $[(\text{C}_6\text{H}_5)(\text{FC}_6\text{H}_4)\text{C}_2\text{Fe}^+]$, and 270 $[(\text{FC}_6\text{H}_4)_2\text{C}_2\text{Fe}^+]$, which give peaks in our instrument at m/e 122.2, 141.7, and ~ 162.7 in agreement with prediction,¹³ are given in Table I. Allowing bond formation between all of

Table I. Metastable Decompositions of $\text{C}_4\text{Ar}_4\text{Fe}^+$ in Spectra of Substituted Tetracyclonetricarbonylirons

	Rel area		
	122.2	141.7	162.7
II	1	1.7	~ 0.5
III	1	170	~ 1
IV	1	2.0	~ 0.5

(5) M. M. Bursey, F. E. Tibbetts, III, W. F. Little, M. D. Rausch, and G. A. Moser, *Tetrahedron Lett.*, 3469 (1969).

(6) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(7) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, P22 (1967).

(8) M. M. Bursey, R. D. Rieke, T. A. Elwood, and L. R. Dusold, *J. Amer. Chem. Soc.*, **90**, 1557 (1968).

(9) M. M. Bursey and T. A. Elwood, *Org. Mass Spectrom.*, **1**, 531 (1968).

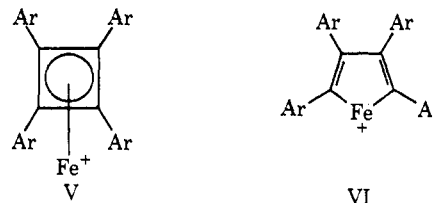
(10) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5307 (1959).

(11) M. I. Bruce, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 335 (1968).

(12) Cf. the remarks on low-intensity precursors by S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Commun.*, 346 (1969), and references contained therein.

(13) Numerous doubly charged ions near m/e 162 make measurement of the maximum and area of the last metastable peak difficult in each case.

the C_4 carbons before fragmentation (as in a tetrahedral arrangement of these ions) would produce intensity ratios of 1:4:1 for the metastable peaks in all three compounds. Alternatively, a square structure should produce relative intensities of 1:2:1 in II and IV but should give only m/e 141.7 in III. The data are obviously in far better accord with the second model than with the first; the C_4 unit is not exactly square, but a tetrahedral structure is not achieved. A consistent model for this ion is therefore V. We might consider VI as a possible structure, if there is random insertion of Fe into the four-membered ring after V is formed, but the symmetry of V is achieved before decomposition.

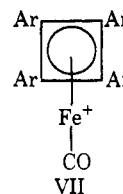


A similar type of scrambling (Table II) was observed for the $[\text{M} - 3\text{CO}]$ ion at m/e 476, which in decomposing to the three possible $\text{C}_2\text{Ar}_2\text{Fe}^+$ ions produces metastable peaks at m/e 115.0 ($476 \rightarrow 234$), 133.4 ($476 \rightarrow 252$), and 153.1 ($476 \rightarrow 270$). The pattern suggests again

Table II. Metastable Decompositions of $\text{C}_4\text{Ar}_4\text{COFe}^+$ in Spectra of Substituted Tetracyclonetricarbonylirons

	Rel area		
	115.0	133.4	153.1
II	1	2.2	~ 0.3
III	1	120	Not detected
IV	1	1.7	~ 0.3

that a planar structure for the C_4 unit is achieved before fragmentation of these ions; a cyclobutadiene form is indicated by the relative intensities of the peaks in II and IV, for the 2 and 5 positions of the cyclopentadienone ring are joined by a bond approximately equal in strength to that between the 3 and 4 carbons. Yet, as the data for III indicate, no bonds between the 2 and 4 positions or between the 3 and 5 positions are formed. One structure for the $[\text{M} - 3\text{CO}]$ ion representing this situation is VII, but an extrusion-reinsertion mechanism where VII is intermediate between forms where CO migrates around the ring could also explain the results.



The possibility also exists that scrambling in the second case explains the first case fully, but there is no interpretation in which stabilization of a cyclobutadiene structure by Fe against further randomization is not cardinal. The apparent symmetry of both sets of ions reflects the established stabilization of cyclobutadiene by iron⁶ and other transition metals.

Acknowledgment. Support of this work by the National Science Foundation (GP 8096, GU 2059) is gratefully acknowledged.

(14) Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.

Maurice M. Bursey,¹⁴ Fred E. Tibbetts, III, William F. Little
Venable Chemical Laboratory, The University of North Carolina
Chapel Hill, North Carolina 27514

Received October 16, 1969

The Role of Coordinated Sulfur in Oxidation–Reduction. I. The Chromium(II) Reduction of Mercaptoacetatobis(ethylenediamine)cobalt(III) and Its Glycollato Analog

Sir:

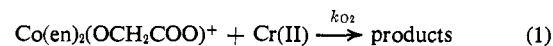
Recent research has revealed a widespread utilization of nonheme iron–sulfur proteins in biological oxidation–reduction processes.¹ Iron, acid-labile sulfur, and thiolate sulfur from cysteine are stoichiometrically and functionally related, implying coordination by sulfur.¹ ESR studies of isotopically substituted samples of a representative two-iron protein indicate that both iron atoms, both acid-labile sulfur atoms, and at least some of the cysteinyl sulfur participate in the redox site.² These developments serve to underscore the lack of quantitative information regarding the influence of coordinated thiolate functions on the rates and mechanisms of oxidation–reduction reactions. We wish to describe a markedly enhanced rate of inner-sphere reduction of a mononuclear cobalt(III) complex arising from replacement of a single coordinated alcoholate oxygen by thiolate sulfur. These represent the first studies of this type of the thiolate and alcoholate functions.

[Co(en)₂OCH₂COO]ClO₄ was prepared by a method analogous to that used for [Co(en)₂(NH₂CH₂COO)]Cl₂.^{3a} Addition of aqueous sodium perchlorate to a solution of the initial product yielded the perchlorate salt which was recrystallized from water. *Anal.* Calcd: C, 20.45; H, 5.15; N, 15.9; Co, 16.7. Found: C, 20.36; H, 5.12; N, 15.7; Co, 16.6 (as Co(tri-pyridine)₂²⁺ after liquid-fire (HNO₃–HClO₄) decomposition). Spectral data were (λ (ε): 5180 (132), 3600 Å (140) in water and 4990 (113), 3480 Å (121) in 0.10 M HClO₄. Intense infrared absorption (in KBr) at 1635 and 1360 cm⁻¹ is characteristic of coordinated carboxylate.³ The failure to incorporate H₂O on recrystallization together with spectral comparison with *cis*-[Co^{III}(NH₃)₄(H₂O)(CH₃COO)](ClO₄)₃ (λ (ε): 5100 (67), 3550 Å (50) in water)⁴ provides assurance that the alcohol function remains coordinated for reasonable periods in acidic or neutral solution. The molar conductance is that expected for

a univalent electrolyte. Spectrophotometric and potentiometric titrations yielded an approximate p*K*_a of 3.0 for the complex at 1.0 M ionic strength and 25°.

[Co(en)₂(SCH₂COO)]ClO₄ was synthesized by a procedure similar to that used to produce CrSH²⁺ in solution.⁵ Cobalt(II) perchlorate, ethylenediamine, and the disulfide of mercaptoacetic acid react in 2:4:1 molar ratios in deaerated water to yield the desired compound which was recrystallized several times from water (λ 5160 Å (ε 149)). *Anal.* Calcd: S, 8.67; C, 19.5; H, 4.88; N, 15.2. Found: S, 8.53; C, 19.5; H, 4.84; N, 15.13. Infrared absorption (KBr) at 1635 and 1340 cm⁻¹ is assigned to coordinated carboxylate, and the absence of S–H absorption at ~2500 cm⁻¹ is indicative of thiolate coordination. This complex is not detectably basic under the conditions studied and, after allowing for the change in sulfur substituent from hydrogen to alkyl, seems comparable to CrSH²⁺ in this sense.⁵ No appreciable spectral change occurs between 10⁻⁷ and 1 M HClO₄. Further, when sufficient complex is brought into 0.1 M HCl solution (by reaction with equivalent (C₆H₅)₄AsCl followed by centrifugation of (C₆H₅)₄AsClO₄) to be 0.1 M in complex, the pH is unchanged from its original value.

Reaction rates with chromium(II) were determined at 25° and 1.0 M ionic strength (LiClO₄–HClO₄) using a Durrum-Gibson stopped-flow spectrophotometer at the low-energy cobalt absorption peak. Co(en)₂(HOCH₂COO)²⁺ is consumed under pseudo-first-order conditions according to the rate law, (38 + 0.99[H₃O⁺]⁻¹)[Cr(II)][Co(III)] (time in seconds), over the ranges 1.0 × 10⁻² M < [Cr(II)] < 5.0 × 10⁻² M and 1.0 × 10⁻² M < [H₃O⁺] < 1.0 × 10⁻¹ M. Elimination of the acid dissociation constant from the value for the inverse acid path yields *k*₀₂ = 990 M⁻¹ sec⁻¹ for reaction of the deprotonated species.



Chromium(II) was found, by spectrophotometry, to consume Co(en)₂(HOCH₂COO)²⁺ in a 1:1 molar ratio over a range of [Co^{III}]:[Cr^{II}] from 0.5 to 2.5 at the 5 × 10⁻³ M level. The product spectrum excludes Cr(H₂O)₆³⁺ as an appreciable product, indicating instead an inner-sphere reaction with the bridging glycollate ligand captured in the inert Cr(III) coordination sphere. A molecular model of the cobalt reactant indicates that the chelate link makes a doubly bridged reaction extremely unlikely for steric reasons. The similar rate constant in the acid-independent path to the *cis*-Co(NH₃)₄(OAc)(H₂O)²⁺–Cr(II) reaction (see Table I), where CrOAc²⁺ is the dominant product,^{4c} and the spectral properties of the products⁶ are consistent with carboxylate bridging for this path although an alcohol bridge has not yet been rigorously excluded. The inverse acid dependence and high rate constant for the second path virtually demand alkoxide bridging.

Reaction of Cr(II) with Co(en)₂(SCH₂COO)⁺ at 0.1 M HClO₄ is complete at the lowest observable equimolar concentrations (5 × 10⁻⁵ M) within the mixing “dead time” of our apparatus. We conservatively estimate *t*_{1/2} < 0.010 sec and, assuming a second-order reaction, calculate *k*_{S₂} > 2 × 10⁶ M⁻¹ sec⁻¹ (25°) for

(5) M. Ardon and H. Taube, *J. Amer. Chem. Soc.*, **89**, 3661 (1967).

(6) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965), present spectral characteristics of Cr(III)–glycollate complexes.

(1) (a) R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967); (b) A. San Pietro in “Biological Oxidations,” T. P. Singer, Ed., Interscience Publishers, New York, N. Y., 1968, p 515.

(2) (a) J. C. M. Tsibris, R. L. Tsai, I. C. Gunsalus, W. H. Orme-Johnson, R. E. Hansen, and H. Beinert, *Proc. Natl. Acad. Sci. U. S.*, **59**, 959 (1968); (b) W. H. Orme-Johnson, R. E. Hansen, H. Beinert, J. C. M. Tsibris, R. C. Bartholomew, and I. C. Gunsalus, *ibid.*, **60**, 368 (1968).

(3) (a) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 1590 (1966); (b) K. Nakamoto, “Spectroscopy and Structure of Metal Chelate Compounds,” K. Nakamoto and P. J. McCarthy, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 268.

(4) (a) R. R. Miller, Ph.D. Thesis, University of Chicago, 1963. We are indebted to Dr. E. Deutsch for forwarding this information. (b) See M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **264**, 321 (1951), for spectral consequences of changing amine functions. (c) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).