Inversion could occur in the interconversion of I and III, or in separate relatively rapid reactions of III or IV (by twist mechanisms, or oxygen–oxygen displacements). It is also reasonable that water addition to III would be rapid, and to some extent competitive with ring closure. Such water addition would result in a stabilized monodentate oxalate ligand and would provide the obvious path toward complete aquation.

Any suggestion that racemization could occur through a twist mechanism in I does not explain the kinetically similar inner-oxygen exchange, nor does it accommodate the beginning of aquation. It has also been suggested that inner–outer oxygen equilibration, for some oxalato complexes, may occur through occasional rotation of oxalate about its carbon–carbon bond. This mechanism is unlikely to be important here, because it does not explain the kinetically similar racemization, or again the beginning of aquation.

The possibility that V forms directly from II should be considered (see Figure 3, arrows in parentheses). Such a process could involve Rh–O or O–C bond cleavage, and in either case we would have an alternate route toward complete aquation. Rhodium–oxygen bond cleavage with entry of solvent water would allow for exchange of the inner oxygen, although in comparison to the mechanism involving III it is much less obvious that inner-oxygen exchange and racemization should be kinetically so similar. Oxygen–carbon bond cleavage does not allow for exchange of inner oxygen, nor is it apparent that racemization would result. In summary, it appears to us that the close coincidence of inner-oxygen exchange and racemization kinetics is much more readily accommodated by the proposed mechanism involving intermediate III.

Acknowledgment. We wish to express our thanks to Professor Richard H. Holm of the Massachusetts Institute of Technology for allowing us to make use of his Perkin-Elmer 141 spectropolarimeter.

no comparable [H^+]-independent term for the racemization of $Rh(C_2O_4)_3^{3-}$ is probably attributable to the greater inertness of the metal–oxygen bonds in this case.

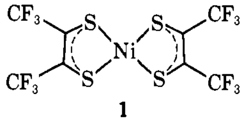
Mechanism of Oxidative Cycloaddition of Olefins to Metal Dithiolenes

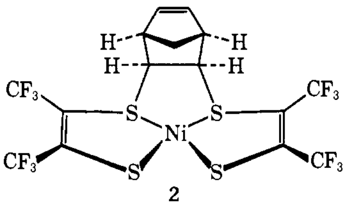
James R. Baker, Alvin Hermann, and Richard M. Wing*

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received February 24, 1971*

Abstract: The strong inorganic oxidant bis[*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)]nickel reacts readily with olefins to form 1:1 adducts in which two new sulfur–carbon bonds have been formed and the olefin becomes the backbone of a new chelate ring. Two classes of behavior have been distinguished by the present studies. First, when a nonconjugated olefin is used, adduct formation (which always obeys a second-order rate law) is slow (~1 l. mol^{-1} sec^{-1} at 25°) and the reaction product dissociates in light to a photostationary state. Second, when a conjugated olefin is used the reaction is very fast (>10^5 l. mol^{-1} sec^{-1} at 25°) and is thermally reversible. These observations are readily explained by a simple orbital correlation model.

A recent attempt to catalyze the valence isomerization, quadricyclene–norbornadiene, with bis-[*cis*(1,2-perfluoromethylethene-1,2-dithiolato)]nickel (**1**) (nickel dithiete) failed largely as the result of **1** reacting with norbornadiene to give the 1,8 cycloaddition product 2.[1] On the basis of structural and spectroscopic results, this reaction has been described as an oxidative cycloaddition.


1


2

Based on recent kinetic, photochemical, and thermodynamic results, we are now able to present a more detailed interpretation of this interesting reaction.

A simple orbital correlation model is presented which concisely explains the nickel dithiete–olefin reactions.

Experimental Section

Preparation of Compounds. $NiS_4C_4(CF_3)_4$ was prepared according to the method of Davison *et al.*,[2] and the norbornadiene adduct according to ref 1. Reagent grade solvents were dried over Linde Type 4A molecular sieves. The microanalysis was carried out by C. F. Geiger, Ontario, California.

The 2,3-Dimethylbutadiene–Bis[*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)]nickel Adduct. Slow diffusion at 5° of a $NiS_4C_4(CF_3)_4$ *n*-hexane solution (100 mg, 0.196 mmol in *ca.* 50 ml) into a CCl_4 solution of the olefin (1 g, 12.2 mmol in 5 ml) gave yellow-green prismatic crystals (82 mg, 71%), mp 153–154° dec. *Anal.* Calcd

---

[1] R. M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, 92, 1935 (1970).

[2] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 2, 1227 (1963).

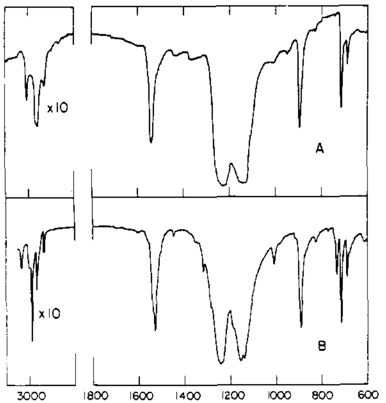


Figure 1. Ir spectra of (A) nickel dithiete–norbornadiene adduct, (B) nickel dithiete-2,3-dimethylbutadiene adduct.

for $C_{14}H_{10}F_{12}S_4Ni$: C, 28.35; H, 1.70. Found: C, 28.31; H, 1.77.

Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer using the KBr pellet method for sample preparation.

Visible Spectra. The visible–near-ir spectra were recorded on Perkin-Elmer Model 450 and Cary Model 14 double-beam spectrometers. The latter instrument was used for the kinetic and equilibrium studies.

Pmr Spectrum. The pmr spectrum of the 2,3-dimethylbutadiene–nickel dithiete complex in deuteriochloroform solution was recorded on a Varian Model A-60D instrument.

Owing to the low solubility of the complex ($\sim 5 \times 10^{-3}$ *M* at $-3°$, the temperature at which the spectrum was recorded owing to the instability of the complex at higher temperatures), the instrument's output signal was averaged by a Varian Model C-1024 time-averaging computer. The sweep was triggered by an internal TMS signal, and 150 averages were required to improve the signal/noise ratio of the sample's weakest resonance to 4:1.

Kinetic Measurements. Solutions containing about 0.08 mg of norbornadiene–nickel dithiete per milliliter ($\sim 1.33 \times 10^{-4}$ *M*) were placed in a thermostated 1-cm quartz cell. Care was taken to prevent exposure of the solution to light. Temperature control to about $\pm 0.05°$ was maintained by means of a Haake Model F thermostat unit coupled with a Brinkman thermoelectric cooling unit. A Leeds and Northup temperature potentiometer fitted with a glass-shielded iron–constantin thermocouple in contact with the solution was used to measure the temperature to 0.1°.

The solution was then photolyzed for about 5 min by exposure to the near-ir tungsten source of the Cary-14. This method, which is remarkably clean, produces equimolar quantities of the reactants, norbornadiene and nickel dithiete. The only known side reaction, one which produces the monoanion of nickel thiete, became evident only after five to eight photolysis–recombination cycles; solutions were therefore discarded after three cycles. The photolysis described above produced about 70% dissociation as indicated by the absorption of the 7195-Å nickel–dithiete band, and it was by monitoring this same band (ϵ 12,700 l. mol^{-1}) that the concentration–time data were collected. The data were analyzed using a least-squares fit to the integrated equations for $2A \rightarrow A_2$.[3] Rate constants from duplicate runs were reproducible to 5%. A summary of the results is given in Table I.

Equilibrium Measurements. Temperature control and measurement were achieved as described above, except for a slight modification required for control below 10°. Between 10 and $-20°$ methanol was first overcooled and then reheated to the desired temperature by the Haake thermostat. Equimolar solutions of nickel dithiete and olefin were made up at *ca.* 2×10^{-4} *M* and the absorbance of the 7195-Å nickel dithiete band was measured. Values of the equilibrium constant were then computed using the derived equation

$$K_{eq} = (C - A/\epsilon l)/(A/\epsilon l)^2$$

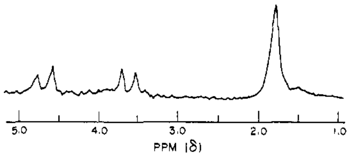


Figure 2. ^1H nmr spectrum of the nickel dithiete-2,3-dimethylbutadiene adduct.

where *C* is the initial nickel dithiete concentration, *l* is the path length of the cell, *A* is the absorbance at 7195 Å, and ϵ is the molar extinction coefficient of nickel dithiete at that wavelength; *vide supra.*

Table I. Nickel Dithiete + Norbornadiene → Adduct

Temp, °C	Rate, l. sec^{-1} M^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal °K^{-1}
	Cyclohexane Solvent		
30.5	1.417	8.638	−29.5
41.0	2.415	8.615	−29.5
52.5	4.395	8.593	−29.8
62.5	6.017	8.573	−29.8
	E_a = 9.24 kcal °K^{-1} mol^{-1}		
	1,1,1-Trichloroethane Solvent		
18.0	2.90	7.868	−35.6
31.2	5.04	7.850	−37.8
40.3	5.44	7.833	−38.8
49.1	10.33	7.815	−40.5
	E_a = 8.455 kcal °K^{-1} mol^{-1}		

Photochemical Measurements. The light source intensities were measured after the photolysis of each sample by replacing the sample with a potassium ferrioxalate chemical actinometer.[4]

A 1-cm quartz cell of 2-ml volume was used as the reaction vessel for both the sample and actinometer.

Two different light sources were used. In the preliminary work a 100-W tungsten lamp was used which was later replaced with a low-pressure mercury arc lamp (Baush and Lomb SP-200). A water-filled 1-l. round-bottomed flask was used to focus the light beam on the cell and to absorb the heat-producing infrared radiation from the sources.

Three different filters were used to select the wavelengths focused on the cell. One was an aqueous solution of $CuSO_4$ (0.44 g/100 ml of 2.7 *M* NH_4OH) which transmits light in the range 3500–4400 Å. The other two were spike filters with λ_{max} 3520 and 4030 Å and band widths of 60 Å (Jenaer Glaswerk, Mainz, West Germany).

The extent of the photolysis was kept small, so that no correction was required for the dark recombination, and was monitored by measuring the absorbance of the 7195-Å band of nickel dithiete on a Beckman DU spectrophotometer. All of the photochemistry was done at 25°.

Results and Discussion

Structure of the Nickel Dithiete–2,3-Dimethylbutadiene Adduct. The infrared spectra of the previously characterized norbornadiene adduct **2** and of the 2,3-dimethylbutadiene adduct **3** (Figure 1) are virtually identical. Prominent characteristics of the spectra are the strong bands at *ca.* 1535 and 900 cm^{-1} which are comparatively weak in the spectrum of nickel dithiete (**1**). These have been assigned as $\nu_{C=C}$ and $\nu_{C=C=S}$, respectively, of the thiete ligand,[5] and we believe their marked increase in intensity to be characteristic of adducts formed by 1,8 addition to the coordinated thiete ligands.

Since it is clear from the nmr spectrum (Figure 2) that the reaction has gone 1,4 with respect to the butadiene,

---

[3] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953.

[4] J. G. Calvert and J. N. Pitts, Jr. "Photochemistry," Wiley, New York, N. Y., 1966, pp 784–786.

[5] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).

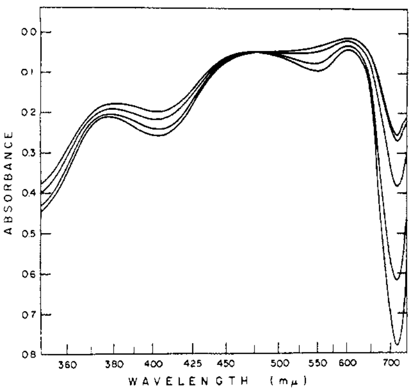
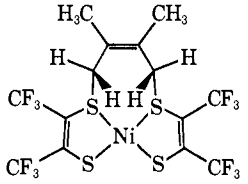


Figure 3. Visible spectra of nickel dithiete and norbornadiene as a function of time at about 29° Note the single isosbestic point at λ 475 mμ.

we assign **3** as the structure of this product. We prefer the exo conformer because of the large chemical



3

shift difference between methylene protons. This structural detail, although not necessary to our interpretation of the reaction mechanism, has been confirmed by X-ray diffraction.[6] The geminal coupling constant derived from the methylene AB pattern (13.5 Hz) is consistent with tetrahedrally hybridized carbon.[7]

Adduct Formation. The cycloaddition reaction was shown to obey second-order kinetics (first order in each reactant) for norbornadiene (Figure 3) and norbornene, with the former substrate being the basis for the bulk of our studies. Conjugated diolefins react so rapidly that kinetics measurements were impossible in most cases. However, substitution of the 1 and 4 positions (*e.g.*, 1,3-cyclohexadiene) slowed the reaction sufficiently that the rate law was verified to be the same as that for unconjugated olefins.

The kinetic data for the nickel dithiete–norbornadiene reaction are summarized in Table I. The entropy term ($\Delta S^{\ddagger}$) is about what is expected for a combination reaction, and the acceleration of the rate in polar solvents is consistent with a charge-separated transition state such as one might expect if the reaction is faithfully described as an oxidative cycloaddition.

Blinn and Busch[8] in their studies of nucleophilic displacement reactions on carbon by coordinated sulfur discovered what they describe as the kinetic chelate effect. This effect makes the chelate-ring-forming second step of reactions of cis dimercapto coordination compounds with alkyl or aryl dihalides very rapid. In effect, the second step appears to be concerted with the initial attack. Our rate data, which greatly resemble those of Blinn and Busch, therefore do not prove concertedness. We feel, however, that the five orders of magnitude difference in rates along with the contrast in photochemistry and thermal behavior (*vide infra*) of the various adducts are strong indications of a concerted pathway, at least for the reaction with conjugated olefins.

Adduct Dissociation. While the adducts with unconjugated olefins are thermally stable, we find the corresponding conjugated-olefin reactions to be thermally reversible.

The formation constant for the 2,3-dimethylbutadiene–nickel dithiete adduct is 1.1 × 10^4 at 25° in hydrocarbon solvents. From the temperature dependence of the equilibrium, we calculate the enthalpy for the reaction to be -17.1 ± 0.2 kcal mol^{-1}, resulting in values for ΔG_{298} and ΔS_{298} of -5.6 kcal/mol^{-1} and -38 eu, respectively.

A crude estimate[9] of the energy of the S–C bond formed in this reaction is then 63 kcal mol^{-1}, which is to be compared with the literature value of 65 kcal mol^{-1}.[10] This value is consistent with the single-bond S–C distances observed in the norbornadiene–nickel dithiete[1] and butadiene–nickel dithiete adducts.[6]

The nonconjugated olefin adducts are light sensitive,[1,5,11] with their solutions dissociating to a photostationary equilibrium if not carefully protected from light. We give in Table II some quantum yields for

Table II. Photolysis of the Adduct to Give Nickel Dithiete + Norbornadiene

λ, Å	Solvent	Φ
Vis region	CCl_4	0.3095
4400–3500	CH_3CCl_3	0.284
	C_6H_{12}	0.280
3500	C_6H_{12}	0.4281
4050	C_6H_{12}	0.3424

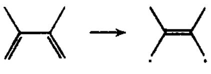
---

[6] Confirmation of the structure **3**, pivotal to our arguments (*vide infra*), has been made by a single-crystal X-ray diffraction study. The current weighted residue is 9.5% with refinement continuing.

[7] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 31, 1278 (1959).

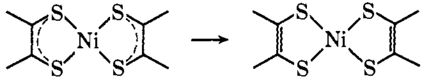
[8] E. L. Blinn and D. H. Busch, *Inorg. Chem.*, 7, 820 (1968).

[9] J. D. Roberts and M. Casario, "Basic Principles of Organic Chemistry," Benjamin, New York, N. Y., 1964. We use the following cycle



(I)

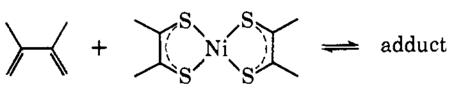
$\Delta H_{\mathrm{I}} = 67$ kcal/mol



(II)

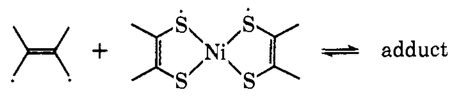
$\Delta H_{\mathrm{II}} = 41$ kcal/mol

The basis for (II) is twice the electronic excitation energy to the first excited singlet state of nickel dithiete.



(III)

$\Delta H_{\mathrm{III}} = -17$ kcal/mol



(IV)

$\Delta H_{\mathrm{IV}} = -125$ kcal/mol

IV = III − I − II.

[10] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[11] G. N. Schrauzer, R. K. Y. Ho, and R. P. Murillo, *J. Amer. Chem. Soc.*, 92, 3508 (1970).

the photolysis of **2**. The process is quite efficient, solvent independent, and not quenched by free radical scavengers. In contrast, the thermal dissociation of **3** is unperturbed by light.

Reaction Mechanism. The contrast in behavior between the nonconjugated and conjugated olefin reactions with nickel dithiete strongly suggests a cycloaddition mechanism in which the former reaction is orbitally forbidden.[12]

The nature of the nickel dithiete reactant, however, does not conform to the requirements for a "by rote application" of the Woodward–Hoffmann reactivity selection rules. Thus we present a scheme for this system, as shown in Figure 4.

Most critical to this correlation is the identification of the lowest lying unfilled orbital of nickel dithiete. We chose the orbital depicted in Figure 4a, based on the elegant esr sulfur hyperfine studies of Schmitt and Maki.[13] Schrauzer and Rabinowitz[14] have done Hückel π molecular orbital calculations which agree with the esr results, and we adopt their coordinate system in describing the orbital. Reference should be made to their paper for further details.

The nonconjugated and conjugated olefin reactions are depicted in Figures 4b and 4c, respectively, with the basis being nonzero overlap between the highest filled orbitals of the olefin and the lowest lying empty orbital of nickel dithiete.

It is clear (Figure 4b) that the ethylene–nickel dithiete interaction shown on the left-hand side of the equation cannot lead to the ground-state adduct. Thus, this reaction must either utilize a higher energy nickel dithiete state or proceed by a nonconcerted process. In either case a slow photoreversible process would be predicted. Interestingly, addition to S(1) and S(4), which is orbitally allowed, does not occur. This can be attributed to the resultant gross disruption of the nickel dithiete π-electron system, as well as the reluctance of a thiete ligand to undergo a two-electron reduction.

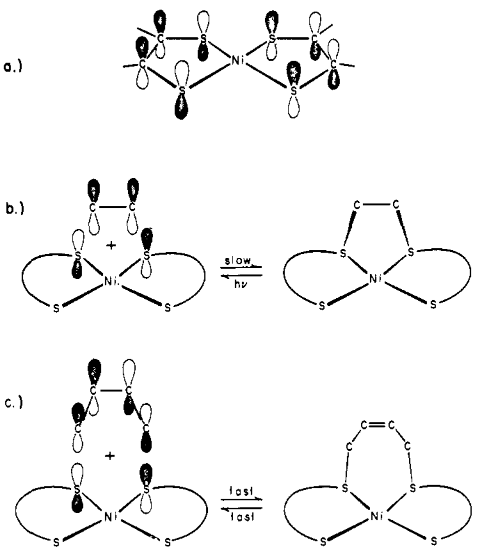


Figure 4. Orbital correlation schemes: (a) lowest lying unoccupied molecular orbital (b_{2g}) of nickel dithiete; (b) orbital correlation for ethylene and nickel dithiete (S(1) and S(8) p orbitals only) showing that the concerted thermal reaction is orbitally forbidden and hence likely to be slow; (c) orbital correlation for 1,3-butadiene and nickel dithiete showing that the concerted thermal reaction is orbitally allowed.

The 1,4 pathway for conjugated olefins is orbitally allowed. Consistent with this is the observed rapid thermal equilibration (Figure 4c). An alternate 1,5 stereochemistry is not observed for steric reasons.

Summary and Conclusions

A simple orbital correlation model provides a straightforward explanation of the reactions of olefins with the strong inorganic oxidant nickel dithiete. Furthermore, this correlation also suggests that the previous description of the reaction as an oxidative cycloaddition is adequate.

Acknowledgments. This work was supported by the National Science Foundation under Grant No. GP-8055.

---

(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

(13) R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, 90, 2288 (1968).

(14) G. N. Schrauzer and H. N. Rabinowitz, *ibid.*, 90, 4297 (1968).