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Kinetics and Mechanism of the Reaction of Nickelocene with Mercaptans

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Received August 19, 1970

The kinetics of the reaction of bis(cyclopentadienyl)nickel with mercaptans to give bis(cyclopentadienyl)di-μ-mercaptodinickel have been studied in cyclohexane, tetrahydrofuran, cumene, and acetonitrile. Rate constants and activation parameters are insensitive to solvent and relatively insensitive to the nature of the mercaptan. For the reaction with thiophenol, $\Delta H^{\ddagger} = 12.7$ kcal/mol and $\Delta S^{\ddagger} = -26$ eu in cyclohexane while $\Delta H^{\ddagger} = 12.9$ kcal/mol and $\Delta S^{\ddagger} = -26$ eu in acetonitrile. Activation parameters for the reaction with cyclohexanethiol in cyclohexane are $\Delta H^{\ddagger} = 11.7$ kcal/mol and $\Delta S^{\ddagger} = -34$ eu. A primary kinetic isotope effect is observed when the rate constant for *S*-deuteriothiophenol is compared to that for thiophenol, $k_H/k_D = 2.8$. With thiophenol in cyclohexane, bis(methylcyclopentadienyl)nickel undergoes the analogous reaction at almost the same rate as unsubstituted nickelocene. The results are interpreted in terms of a mechanism proposed by Ustynyuk, *et al.*, in which a π–σ cyclopentadienyl rearrangement accompanies nucleophilic attack by mercaptan at nickel.

Introduction

The kinetics of reactions in which the cyclopentadienyl ligand functions as an entering or leaving group in a transition metal complex have not been extensively studied. Such mechanistic conclusions as have been drawn have been based on inferences from synthetic more often than kinetic studies, frequently relying on the postulate[1] that metal–cyclopentadienyl σ bonds are more readily cleaved than metal–cyclopentadienyl π bonds. For a number of transition metal complexes containing unsaturated ligands, firm evidence exists for σ–π isomerizations.[2] Of particular interest is recent evidence that tris(σ-cyclopentadienyl)iron is an intermediate in the formation of ferrocene from sodium cyclopentadienide and ferric chloride.[3]

Similarly, it has been argued that phosphines interact with nickelocene to give adducts in which one of the cyclopentadienyl groups has undergone a π to σ rearrangement. This proposal[4] is supported by isolation of the appropriate products from reaction mixtures containing reagents known to cleave metal–carbon σ bonds. Thus, either from nickelocene and triphenylphosphine or from (π-C_5H_5)Ni(Cl)P(C_6H_5)$_3$ and sodium cyclopentadienide, an unstable species is formed which yields (π-C_5H_5)Ni(X)P(C_6H_5)$_3$ (X = Cl, I) on treatment with carbon tetrachloride, hydrogen chloride, or iodine. The composition of this species is presumed[4] to be Ni(C_5H_5)$_2$P(C_6H_5)$_3$. Since, on treatment with either carbon tetrachloride[4] or iodine,[5] the nickel–carbon σ bond in (π-C_5H_5)Ni(CH_3)P(C_6H_5)$_3$ is readily cleaved to give (π-C_5H_5)Ni(X)P(C_6H_5)$_3$, Ustynyuk, *et al.*, inferred that Ni(C_5H_5)$_2$P(C_6H_5)$_3$ contains a σ-bonded cyclopentadienyl group.

Ustynyuk, *et al.*, proposed that π to σ rearrangement of a cyclopentadienyl ligand is a general mechanistic characteristic of reactions in which nickelocene experiences nucleophilic attack. Corroborative evidence for this postulate in the case of phosphorus donor ligands has been provided by a kinetic study[6] of the reaction of triethyl phosphite with nickelocene to give tetrakis(triethyl phosphite)nickel(0). Here the rate law is found to be first order in nickelocene and second order in triethyl phosphite, strongly implying the presence of a 1:1 adduct, whose further reaction with a second molecule of triethyl phosphite is rate determining. At low temperatures spectroscopic evidence for the presence of such an adduct is observed.[6]

The reaction of bis(cyclopentadienyl)di-μ-carbonyldinickel with monodentate ligands to give nickelocene and diliganddicarbonylnickel has been the subject of a recent kinetic study.[7] While this study provided limited information on the intimate reaction mechanism, the results are compatible with a rearrangement of the type proposed by Ustynyuk (for the reverse reaction).

Nickelocene has been shown[8] to react readily with mercaptans according to (1) to give bis(cyclopentadienyl)di-μ-mercaptodinickel and cyclopentadiene (*vide infra*). Since this reaction proceeds smoothly and quantitatively and the ultimate fate of the displaced

$$\mathrm{Ni(C_5H_5)_2 + 2RSH \longrightarrow 2C_5H_6 + Ni_2(C_5H_5)_2(SR)_2} \qquad (1)$$

cyclopentadienyl moiety is clear, it seems particularly suitable for kinetic study.

Experimental Section

All operations involving air-sensitive materials were carried out under an atmosphere of argon or prepurified nitrogen.[9] Microanalyses were performed by C. F. Geiger, Ontario, Calif., or Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials.—Nickelocene and the mercaptans were obtained commercially. Nickelocene was dissolved in toluene at room temperature and recrystallized at −78°. Thiophenol and benzyl mercaptan were fractionally distilled at reduced pressure while 2-naphthalenethiol was sublimed at reduced pressure and 80° onto a surface at room temperature. The *p*-chloro- and *p*-methyl-substituted thiophenols were sublimed at room temperature and reduced pressure onto a surface maintained at −78°. Commercially obtained cyclohexanethiol required no further purification. "Nanograde" acetonitrile (Mallinckrodt Chemical

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(1) B. F. Hallum and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

(2) The subject of σ–π rearrangements in transition metal complexes was recently reviewed: M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Angew. Chem.*, **81**, 453 (1969).

(3) M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *J. Amer. Chem. Soc.*, **91**, 5233 (1969).

(4) Y. A. Ustynyuk, T. I. Voevodskaya, N. A. Zharikova, and N. A. Ustynyuk, *Dokl. Chem.*, **181**, 640 (1968).

(5) H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometal. Chem.*, **6**, 86 (1966).

(6) H. Werner, V. Harder, and E. Deckelmann, *Helv. Chim. Acta*, **52**, 1081 (1969).

(7) P. C. Ellgen, *Inorg. Chem.*, **10**, 232 (1971).

(8) W. K. Schropp, *J. Inorg. Nucl. Chem.*, **24**, 1688 (1962).

(9) D. F. Shriver, "The Manipulation of Air-sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapter 7.

Works) was distilled in an atmosphere of nitrogen. Other solvents were refluxed over calcium hydride and distilled in a nitrogen atmosphere. Deuterium oxide (99.8%) was used as received. Sodium hydride was purchased as a 59% oil dispersion and freed of oil before use by washing with dry hexane.

Preparation of *S*-Deuteriothiophenol.—Freshly distilled thiophenol (10 ml) was equilibrated with six successive 10-ml portions of D_2O. Each equilibration was effected by vigorously shaking the heterogeneous mixture in a separatory funnel, allowing the two phases to separate, and draining off the used aqueous phase. Finally, the *S*-deuteriothiophenol was dried by filtration through a bed of anhydrous Na_2SO_4. Approximately 6 ml of *S*-deuteriothiophenol was recovered.

The isotopic purity of this material was evaluated by an isotope dilution procedure. An isotopically diluted solution was prepared by mixing 0.156 g (1.42 mmol) of thiophenol of normal isotopic composition with 0.938 g (8.44 mmol) of S-deuterated material. The heights of the pmr thiol resonances for diluted and undiluted *S*-deuteriothiophenol were then compared in identical sample tubes with identical instrument settings. As a check, the sample tubes were cleaned and dried and each was refilled with the other of the two solutions. The pmr spectra were then compared a second time. Both comparisons gave a ratio of 0.295 from which the undiluted material was found to be 94.3% *S*-deuteriothiophenol.

Preparation of Bis(methylcyclopentadienyl)nickel.—Bis(methylcyclopentadienyl)nickel, 1,1′-dimethylnickelocene, was prepared by modification of the published procedures.[10] To a vigorously stirred suspension of 14.1 g (0.59 mol) of sodium hydride in THF, 60 ml (0.6 mol) of freshly cracked methylcyclopentadiene was added dropwise over 60 min. When hydrogen evolution was complete, 100 g (0.22 mol) of dichlorotetrapyridinenickel(II) was added. This mixture was vigorously stirred under reflux for 2.5 hr. Solvent was then evaporated in a water aspirator vacuum. The oily, dark green, crude product was taken up in a minimum of hexane at room temperature. The hexane solution was filtered and cooled slowly to −78° depositing large, dark green crystals which were recovered, washed with additional cold hexane, and dried under vacuum. A second recrystallization effected in the same manner yielded 22 g (46%) of 1,1′-dimethylnickelocene. *Anal.* Calcd for $C_{12}H_{14}Ni$: C, 66.44; H, 6.51. Found: C, 66.39; H, 7.09.

Preparation of $Ni_2(C_5H_4CH_3)_2(SC_6H_5)_2$ and $Ni_2(C_5H_5)_2(SR)_2$.—Bis(methylcyclopentadienyl)di-μ-thiophenolato-dinickel and the bis(cyclopentadienyl)di-μ-mercapto-dinickel complexes from thiophenol, *p*-methyl- and *p*-chlorothiophenol, cyclohexanethiol, benzyl mercaptan, and 2-naphthalenethiol were prepared according to (1) by mixing the appropriate reagents in hexane. In a typical preparation 2 g (10.3 mmol) of nickelocene was dissolved in 50 ml of hexane. To this solution was added *ca.* 12 mmol of the mercaptan; the reaction mixture was then allowed to stand 20 hr at room temperature. Cooling this solution to −78° precipitated the product as black or dark brown crystals which were further purified by recrystallization from hexane. *Anal.* Calcd for $Ni_2(C_5H_5)_2(SC_6H_5)_2$ (mp 124–126°, lit.[8] mp 125°), $C_{22}H_{20}Ni_2S_2$: C, 56.71; H, 4.33. Found: C, 56.85; H, 4.65. Calcd for $Ni_2(C_5H_5)_2(SC_6H_4CH_3)_2$ (mp 127–129°), $C_{24}H_{24}Ni_2S_2$: C, 58.35; H, 4.90. Found: C, 58.73; H, 4.93. Calcd for $Ni_2(C_5H_5)_2(SC_6H_4Cl)_2$ (mp 164°), $C_{22}H_{18}Cl_2Ni_2S_2$: C, 49.41; H, 3.39; Cl, 13.26. Found: C, 49.72; H, 3.29; Cl, 13.30. Calcd for $Ni_2(C_5H_5)_2(SC_6H_{11})_2$ (mp 152–154°), $C_{22}H_{32}Ni_2S_2$: C, 55.28; H, 6.75. Found: C, 54.97; H, 6.32. Calcd for $Ni_2(C_5H_5)_2(SCH_2C_6H_5)_2$ (mp 149–150°), $C_{24}H_{24}Ni_2S_2$: C, 58.35; H, 4.90; Ni, 23.77. Found: C, 58.13; H, 4.99; Ni, 24.03. Calcd for $Ni_2(C_5H_5)_2(SC_{10}H_7)_2$ (mp 198°), $C_{30}H_{24}Ni_2S_2$: C, 63.65; H, 4.27. Found: C, 63.92; H, 4.40. Calcd for $Ni_2(C_5H_4CH_3)_2(SC_6H_5)_2$ (mp 61–62°), $C_{24}H_{24}Ni_2S_2$: C, 58.35; H, 4.90. Found: C, 58.52; H, 4.85.

Gas Chromatographic Detection of Cyclopentadiene.—To 0.58 g (3.1 mmol) of nickelocene covered with 5 ml of toluene was added 0.70 g (6.3 mmol) of thiophenol. After 30 min, a 1-μl portion of the resulting solution was injected into an Aerograph Autoprep 700 gas chromatograph (0.25 in. × 2.5 ft diethylene glycol adipate on 60/80 firebrick). The injection port temperature was 120°, while the column was maintained at 44°. Under these conditions, a peak of retention time 1.4 min was readily observed. No further separation was achieved; the remaining components of the reaction mixture eluted as a single, broad peak whose retention time was 17 min. Authentic, freshly cracked cyclopentadiene exhibited a retention time identical with that of the volatile component of the reaction mixture. When dicyclopentadiene was injected as a 1.1 *M* toluene solution, only the single, broad peak of long retention time was observed; dicyclopentadiene was not cracked to monomer under the chromatography conditions. Similarly, injection of a 1.5 *M* toluene solution of thiophenol resulted only in a single, broad peak of long retention time.

Kinetic Runs.—Nickelocene solutions were prepared by dissolving a weighed quantity of nickelocene in a known volume of solvent, delivered by pipet. Stock solutions of the mercaptans were prepared in volumetric flasks which had been modified to permit exclusion of atmospheric oxygen by provision of an inlet tube for a countercurrent of inert gas. Using these flasks a known mass of mercaptan was readily diluted to a known volume of solution. A reaction was initiated by mixing carefully measured (pipet or syringe) volumes of previously thermostated solutions in a Schlenk tube. An aliquot was transferred, under nitrogen, to a special cell (*vide infra*) which was then sealed to protect the sample from atmospheric oxygen. The cell was then placed in a thermostated cell holder in a Cary 14 spectrophotometer and the absorbance of the solution was monitored as a function of time.

Evaluation of k_D from observed pseudo-first-order rate constants, k_{obsd}, was effected using the relationship $k_{obsd} = k_H[C_6H_5SH]_0 + k_D[C_6H_5SD]_0$ and the independently determined value of k_H. This was justified even though some of the experiments were carried out under circumstances where $[Ni(C_5H_5)_2]_0 \approx [C_6H_5SH]_0$. Since only *ca.* 15% of the nickelocene reacted with C_6H_5SH rather than C_6H_5SD, the largest change in $[C_6H_5SH]$ in any of the kinetic runs was less than $0.15[C_6H_5SH]_0$. Otherwise, rate constants were evaluated graphically in the usual manner.

Spectrophotometric Measurements.—All spectra and absorbance *vs.* time data were recorded with solutions protected from atmospheric oxygen by the use of specially constructed cells. These cells were made from lengths of rectangular Pyrex tubing by sealing one end and fusing a stopcock to the other. When attached to a filling adaptor[11] with a short length of Tygon tubing, these cells were readily purged of oxygen and filled with the desired solution by means of a syringe needle inserted through the bore of the stopcock. The optical properties of these cells were poor. This was not a source of difficulty, however, since all spectra for comparative purposes were recorded using the same cell.

That reactions occurred quantitatively according to (1) was verified by comparison of the visible spectra of reaction mixtures after long times to the spectra of the appropriate authentic complex. When oxygen was rigorously excluded from reaction mixtures or when an excess of nickelocene was used, excellent agreement between product spectra and expectations based on (1) was observed. Some difficulty was experienced in some experiments with excess mercaptan. If oxygen was not rigorously excluded, the absorbance of the reaction mixture eventually became larger, throughout most of the visible region, than appropriate for quantitative reaction according to (1). This effect apparently arose in proportion to the extent of oxygen contamination and may possibly have been due to formation of polymeric mercaptonickel species.[12] In consequence of this effect, some attempted kinetic runs failed to show a satisfactorily stable infinite-time absorbance. Data from these runs were discarded.

Visible spectra for all of the product complexes were similar with intense absorption maxima near 500 and 385 mμ. In most of the kinetic runs, the absorbance of the reaction mixture was monitored at 570 mμ since this minimized the difficulties arising from incomplete exclusion of oxygen.

Results

The reactions of nickelocene with mercaptans according to (1) follow a rate law which is first order in each reagent (eq 2). With thiophenol, 1,1′-dimethylnickelocene undergoes the corresponding reaction according to a rate law of the same form. Rate constants and acti-

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[10] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959); M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

[11] Reference 9, p 151.

[12] P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, **87**, 5251 (1965).

vation parameters obtained are reported in Tables I and II. In general these results are characterized by

$$\frac{d[Ni(C_5H_5)_2]}{dt} = -k[Ni(C_5H_5)_2][RSH] \qquad (2)$$

insensitivity to the substituent variations effected.

TABLE I
RATE CONSTANTS OBSERVED FOR
$2NiCp_2{}^a + 2RSH \longrightarrow Ni_2Cp_2(SR)_2 + 2CpH$

Thiol	$10^4C_{Ni(C_5H_5)_2}$, M	10^2C_{thiol}, M	Temp, °C	Sol-vent^b	10^3k, M^{-1} sec^{-1}
C_6H_5SH	9.1	11.6	30	C	9.4
C_6H_5SH	4.6	11.6	30	C	11.1
C_6H_5SH	6.1	7.8	30	C	11.9
C_6H_5SH	9.1	5.3	30	C	11.2
C_6H_5SH	9.1	2.05	30	C	11.0
C_6H_5SH	4.6	0.61	30	C	9.8
C_6H_5SH	8.4	8.8	30	C	10.5^c
C_6H_5SH	12.3	0.448	30	C	10.5^d
C_6H_5SH	15.4	0.224	30	C	11.0^d
C_6H_5SH	6.1	7.8	40	C	22.4
C_6H_5SH	4.6	4.2	40	C	21.8
C_6H_5SH	8.3	0.77	40	C	22.1
C_6H_5SH	4.6	4.2	50	C	42
C_6H_5SH	8.3	0.81	50	C	45
C_6H_5SH	3.2	14.4	30	T	6.0
C_6H_5SH	4.8	10.8	30	T	6.2
C_6H_5SH	8.6	2.14	30	T	6.0
C_6H_5SH	6.4	7.2	30	T^e	5.9
C_6H_5SH	11.8	30.4	30	A	8.1
C_6H_5SH	7.6	15.4	30	A	8.2
C_6H_5SH	10.0	4.6	30	A	7.9
C_6H_5SH	11.6	18.2	30	A^f	8.1
C_6H_5SH	9.8	15.2	30	A^g	7.8
C_6H_5SH	9.6	48	40	A	17.1
C_6H_5SH	9.9	33	40	A	17.3
C_6H_5SH	10.1	20.3	50	A	32
C_6H_5SH	10.1	20.3	50	A	31
C_6H_5SH	10.1	20.9	50	A	31
C_6H_5SH	24	9.7	30	K	11.0
C_6H_5SH	22	8.4	30	K^h	11.2
C_6H_5SH	24	9.7	30	K^i	10.3
C_6H_5SD	10.1	20.2^j	30	C	3.8
C_6H_5SD	10.1	19.5^j	30	C	4.2
C_6H_5SD	10.1	10.1^j	30	C	3.7
C_6H_5SD	10.1	9.8^j	30	C	3.3
C_6H_5SD	9.3	1.85^j	30	C	4.5
C_6H_5SD	8.5	1.44^j	30	C	3.7
p-ClC_6H_4SH	3.0	10.0	30	C	13.8
p-ClC_6H_4SH	4.6	7.5	30	C	13.7
p-ClC_6H_4SH	6.1	5.0	30	C	14.5
p-ClC_6H_4SH	8.3	1.36	30	C	12.7
p-$CH_3C_6H_4SH$	3.0	9.9	30	C	13.6
p-$CH_3C_6H_4SH$	4.6	7.4	30	C	12.1
p-$CH_3C_6H_4SH$	6.1	4.9	30	C	14.0
p-$CH_3C_6H_4SH$	7.6	2.47	30	C	13.7
$C_6H_{11}SH$	7.7	126	30	C	0.87
$C_6H_{11}SH$	3.8	69	30	C	0.81
$C_6H_{11}SH$	7.0	12.6	30	C	0.90
$C_6H_{11}SH$	3.8	7.1	30	C	0.76
$C_6H_{11}SH$	7.7	126	40	C	1.52
$C_6H_{11}SH$	3.8	69	40	C	1.96
$C_6H_{11}SH$	7.0	12.6	40	C	1.63
$C_6H_{11}SH$	14.1	115	50	C	3.0
$C_6H_{11}SH$	5.1	46	50	C	3.0
$C_6H_5CH_2SH$	5.6	16.5	30	C	6.3
$C_6H_5CH_2SH$	8.4	12.4	30	C	5.4
$C_6H_5CH_2SH$	15	2.26	30	C	6.2
$C_{10}H_7SH$	2.8	19.1	30	C	14.2
$C_{10}H_7SH$	8.4	11.4	30	C	11.7
$C_{10}H_7SH$	15.2	2.08	30	C	13.3
C_6H_5SH	2.7^k	12.5	30	C	15.7
C_6H_5SH	4.1^k	9.4	30	C	15.1
C_6H_5SH	7.6^k	1.22	30	C	14.0

[a] Except as otherwise indicated $NiCp_2$ = bis(cyclopentadienyl)nickel. [b] A = acetonitrile, C = cyclohexane, T = tetrahydrofuran, K = cumene. [c] Light excluded (see text). [d] Rate constants calculated from integrated second-order rate equation. [e] Solution also contained 0.032 M pyridine (see text). [f] Solution also contained 0.12 M $[N(n\text{-}C_4H_9)_4]Br$. [g] Solution also contained 0.20 M $[N(n\text{-}C_4H_9)_4]Br$. [h] Solution also contained 0.80 M diphenylmethane. [i] Solution also contained 0.18 M triphenylmethane. [j] Total thiophenol concentration $[C_6H_5SH]_0 + [C_6H_5SD]_0$; calculation of rate constant as described in text. [k] Bis(methylcyclopentadienyl)nickel.

TABLE II
SUMMARY OF RATE CONSTANTS AND ACTIVATION PARAMETERS FOR
$2NiCp_2{}^a + 2RSH \longrightarrow Ni_2Cp_2(SR)_2 + 2CpH$

Thiol	Sol-vent^b	10^3k, M^{-1} sec^{-1} 30°	40°	50°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
C_6H_5SH	C	10.7	22.1	43	12.7 ± 0.5	−26 ± 2
C_6H_5SH	K	11.0	...	...	...	...
C_6H_5SH	T	6.1	...	...	...	...
C_6H_5SH	A	8.1	17.2	31	12.9 ± 1	−26 ± 4
C_6H_5SD	C	3.85	...	...	...	...
p-ClC_6H_4SH	C	13.7	...	...	...	...
p-$CH_3C_6H_4SH$	C	13.4	...	...	...	...
$C_6H_{11}SH$	C	0.84	1.7	3.0	11.7 ± 1	−34 ± 4
$C_6H_5CH_2SH$	C	6.0	...	...	...	...
$C_{10}H_7SH$	C	13.1	...	...	...	...
$C_6H_5SH^c$	C	14.9	...	...	...	...

[a] Except as otherwise indicated $NiCp_2$ = bis(cyclopentadienyl)nickel. [b] A = acetonitrile, C = cyclohexane, T = tetrahydrofuran, K = cumene. [c] Bis(methylcyclopentadienyl)nickel.

The reaction of nickelocene with thiophenol was followed in tetrahydrofuran, cumene, and acetonitrile as well as cyclohexane. The more polar solvents result in only a slight decrease in the rate constant; the activation parameters in acetonitrile and cyclohexane are virtually identical (Table II). Moreover, the rate constant in acetonitrile is independent of added tetra-n-butylammonium bromide to within experimental error (Table I). These results suggest that little charge development occurs in the transition state of the reaction. In particular, the fact that the entropy of activation is the same in acetonitrile as in cyclohexane strongly implies that the notably negative values are associated with reduced freedom of motion in the activated complex itself and not with solvent structuring by a polar activated complex.[13]

The comparison of rate constants for the reactions of thiophenol and S-deuteriothiophenol with nickelocene is particularly useful. The effect observed, k_H/k_D = 2.80 ± 0.4, must be considered a primary kinetic isotope effect, indicating that sulfur–hydrogen bond breaking occurs in the rate-determining step.[14]

In most kinetic runs, the reaction mixture was continuously exposed to the spectrometer light beam. Identical results were obtained from an experiment in which the sample was exposed to the beam for only a few short intervals.

The reaction of nickelocene with thiophenol was studied in cumene and cumene solutions of di- and triphenylmethane in an effort to observe a rate effect which would suggest the involvement of mercaptyl radicals in the mechanism of (1). The phenylmercaptyl radical has been shown to abstract hydrogen atoms from diphenylmethane.[15] No effect was observed; in all cases the rate constant obtained was essentially the same as that in cyclohexane.

Attempts to follow the reaction of nickelocene with thiophenol in tetrahydrofuran in the presence of added

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[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1963, pp 131–142.

[14] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960; K. B. Wilberg, *Chem. Rev.*, **55**, 713 (1955).

[15] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 4435 (1955).

acid or base failed to provide any information on the nature of the hydrogen-transfer step. In the presence of added *p*-toluenesulfonic acid, both nickelocene and the product decomposed to colorless materials. On the other hand pyridine caused a negligibly small effect on the *rate* at which the absorbance of the solution increased, but the infinite-time spectrum was not that of bis(cyclopentadienyl)di-μ-thiophenolato-dinickel.

Evidence indicating rapid formation of a nickelocene–mercaptan adduct prior to the rate-determining step of (1) would have valuable mechanistic implications (*vide infra*). On the hypothesis that a dialkyl sulfide would have coordinating capabilities comparable to those of a mercaptan but a greatly reduced tendency to give mercaptonickel complexes, cyclohexane solutions of nickelocene containing high concentrations (1–3 *M*) of diethyl sulfide were prepared and their visible spectra examined. Freshly prepared solutions gave no evidence of any reaction. However, on standing for 1 day, these solutions slowly darkened, becoming yellow-brown. The reaction responsible for the slow color change has not been identified.

Discussion

While no direct experimental support has been obtained for a monomeric species, $Ni(C_5H_5)(SR)$, the available evidence indicates that this species is a good *model* for the initial product for reaction 1.

The rate law requires a mechanism in which formation of the dinuclear complex follows the rate-determining step. The magnitude of the kinetic isotope effect observed in the reaction of nickelocene with thiophenol indicates that hydrogen transfer from the mercaptan to nickelocene occurs in the rate-determining step of (1). In principle, hydrogen transfer could precede, accompany, or follow formation of the nickel–sulfur bond. If it is supposed that hydrogen transfer precedes formation of the nickel–sulfur bond, proton transfer and hydrogen atom transfer are distinguishable possibilities. The kinetic isotope effect cannot discriminate among these possibilities.

However, the possibility that either homolytic or heterolytic sulfur–hydrogen bond breaking precedes nickel–sulfur bond formation is unlikely in view of the minimal dependence of the rate constants on the nature of the mercaptan. Were the rate step to produce either a mercaptyl radical or a mercaptide ion, a kinetic dependence on the stability of the radical or anion would be anticipated. While it might be argued that such a dependence is responsible for the fact that cyclohexanethiol reacts only $^1/_{15}$ as fast as 2-naphthalenethiol, the minimal spread of rates observed for 2-naphthalenethiol, the thiophenols, and benzyl mercaptan is incompatible with this expectation. A more plausible explanation for the relative slowness of the reaction with cyclohexanethiol is that nickel–sulfur bond formation precedes or accompanies hydrogen transfer and that steric effects hinder this attack more in the case of cyclohexanethiol than in the cases of the other mercaptans.

That the reaction rate is unaffected by the presence of hydrogen atom donors constitutes additional evidence against formation of mercaptyl radicals in the rate-determining step. The possibility that a proton transfer precedes nickel–sulfur bond formation is further excluded by the evidence against a polar transition state (*vide supra*). It is concluded, therefore, that hydrogen transfer accompanies or follows formation of the nickel–sulfur bond.

In view of this conclusion, the fact that the acidic hydrogen from the mercaptan ultimately appears in the cyclopentadiene produced, and the absence of any evidence for any intermediate hydride species, it is presumed that hydrogen transfer occurs directly to the cyclopentadienyl ligand rather than by way of a species containing a nickel–hydrogen bond. On this basis a cyclopentadienyl ligand is converted to cyclopentadiene in the rate-determining step, and its maximal further influence on the course of the reaction can be only to stabilize the $Ni(C_5H_5)(SR)$ moiety for the brief period required to effect the dimerization. In this sense, then, $Ni(C_5H_5)(SR)$ is a good model for the initial product.

In the cases of nucleophilic attack on nickelocene by phosphorus donor ligands studied by Ustynyuk and by Werner, the results plausibly support the dual postulates of an adduct of significant lifetime and a σ-bonded role for one of the cyclopentadienyl ligands in this adduct. The kinetic results reported here are readily interpreted in terms of the formation of an analogous adduct with mercaptans. Figure 1 summarizes these proposals.

Certain qualifications must be noted, however. In the present case there is no evidence to require that the bracketed structure represent a *bona fide* intermediate in the sense of transition-state theory. That is, it is possible that the bracketed structure merely represents the transition state in a fully concerted process which leads directly to monomeric $(C_5H_5)Ni(SR)$. Moreover, the postulated π–σ cyclopentadienyl rearrangement is justified primarily by analogy to the work of Ustynyuk, *et al.* Particularly if expulsion of cyclopentadiene is a fully concerted process, a transition-state structure in which the cyclopentadienyl moiety is bound in a π-allylic fashion, or as a monoolefin, cannot be excluded on the basis of the available evidence.

Despite these necessary qualifications, the mechanism of Figure 1 gives an excellent account of the kinetic data. As emphasized by Hammond,[16] the question of whether a particular structure represents an intermediate or a transition state is less important than the overall mechanistic appreciation which the structure affords. That is, since the potential intermediate is of high energy, it is a good representation for the transition state for its further reaction. The bracketed

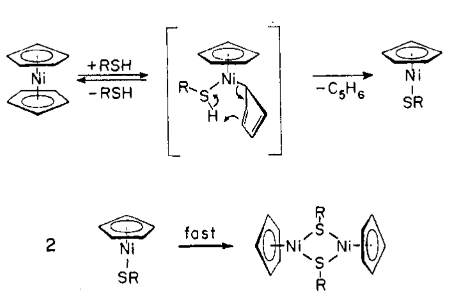

Figure 1.—Proposed mechanism for the reaction of nickelocene with mercaptans.

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[16] G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

structure permits a ready rationalization for all of the available data.

Since retrodative nickel to sulfur electron donation is possible, this structure need exhibit little charge separation. Thus, the insensitivity of rate constants and activation parameters to the polarity of the medium is accommodated. The substantial, negative activation entropy is compatible with the restrictive geometry required for the hydrogen transfer to take place. Less compellingly, rationalization of the smallness of changes in rate constants resulting from variations in the mercaptan is possible. The greater the nucleophilic character of the mercaptan, the stronger should be the nickel–sulfur bond in the activated complex. Simultaneously, however, sulfur–hydrogen bond breaking should be rendered more difficult. Thus changing the nature of the mercaptan might be expected to have a small net effect on the stability of the transition state.

Acknowledgments.—Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. C. D. G. thanks the National Science Foundation for summer fellowship support under the Undergraduate Research Participation program. It is a pleasure to acknowledge helpful discussions with Professors R. C. Neuman and H. W. Johnson.

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The Single-Crystal Polarized Spectrum of Bis(benzoylacetonato)copper(II). Sources of Intensity[1a]

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Received June 4, 1970

The single-crystal polarized spectrum of bis(benzoylacetonato)copper(II) is reported. The "d–d" bands peak at {14.2}, {15.6}, and {18.1} kK, all are predominantly y polarized, and their temperature dependence and relative polarization suggest their assignment as $\{A_g(3z^2 - r^2)\}$, $\{A_g(x^2 - y^2)\}$, and $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy)$, respectively. The relatively high intensity of the spectrum in y polarization in this and other similar complexes is apparently caused because the bulk of the intensity of the "d–d" bands is borrowed from a single charge-transfer state of B_{3u} symmetry. This B_{3u} state, which may lie at considerably lower energy than other u states which can mix with the d states, is probably that in which an electron is transferred from an orbital derived from "lone-pair" orbitals on the oxygen atoms to the $B_{1g}(xy)$ orbital on the copper ion.

Introduction

The sources of optical intensity as well as the identification of the various d–d transitions in copper β-keto-enolates and related systems have been subjects of considerable speculation and some controversy.[2–8] Early attempts to analyze the electronic spectrum of single crystals of copper acetylacetonate ($Cu(acac)_2$) in polarized light were rendered unsuccessful by the unfortunate mode of packing of molecules in the crystal.[4] Moreover, although most workers agreed that the transition intensities are gained by a vibronic mechanism, the manner in which this mechanism works to provide rather strongly polarized bands had not been understood.[4–7] Workers generally either resorted to an unfounded simplified assumption—conspicuously, the idea that only one or a few of the vibrational modes promote all the intensity—or else regarded the problem as being mired in hopeless complexity.

To overcome difficulties associated with the special crystal packing of $Cu(acac)_2$ and to probe details of the practical operation of the intensity mechanism, we undertook structure determination and temperature-dependent polarized spectroscopy on two copper β-keto-enolates—bis(3-phenyl-2,4-pentanedionato)copper(II) ($Cu(3\text{-}phacac)_2$) and bis(benzoylacetonato)copper(II) ($Cu(benzac)_2$). The spectral study on $Cu(3\text{-}phacac)_2$[2] revealed four "d–d" bands and showed them to be vibronically induced and single molecule in origin. The striking overall y polarization of all the bands suggested that the principal source of intensity was the lending (induced by several odd vibrations of various symmetry types) of some of the intensity of a single y-polarized charge-transfer band ($B_{3u} \leftarrow B_{1g}$ in D_{2h}) to each of the d–d bands. The temperature dependence of the spectra implied that the two lower-energy bands were probably $A_g(x^2 - y^2, 3z^2 - r^2) \leftarrow B_{1g}(xy)$ and the two higher energy bands $B_{2g}(xz)$ and $B_{3g}(yz) \leftarrow B_{1g}(xy)$. The predominance of y polarization in the spectra of two other copper β-keto-enolates has been demonstrated,[6] but without temperature dependence data the mechanism and energy level assignments had to be quite speculative. Some experimental problems with the $Cu(3\text{-}phacac)_2$ crystals[2] had led to unreliable features (no-

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(1) (a) Supported by ARPA, SD-131, through the Materials Research Laboratory, by an NSF grant, and by the University of Illinois Graduate Research Board. (b) ICI Postdoctoral Fellow at Oxford, 1968–1970.

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