Dreyfus Foundation Teacher-Scholar Award to I.R.E., and by NIH Research Grant GM 08893.

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Oxidative Addition of Aryl Carboxylates to Ni(0) Complexes Involving Cleavage of the Acyl-O Bond

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Received January 2, 1980

Abstract: Reactions of aryl carboxylates RCOO-*p*-C_6H_4X (R = CH_3, C_2H_5, *n*-C_3H_7; X = H, CH_3, OCH_3, CN) with bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, in the presence of phosphine ligands yield olefin (R(−H)), *p*-XC_6H_4OH, and nickel carbonyl complex(es) when the R group has a β hydrogen, whereas CH_4, C_2H_6, nickel carbonyl complex(es), and nickel phenoxide are formed when the R group is CH_3. The formation of the products is accounted for by assuming oxidative addition of the ester to nickel involving the cleavage of the acyl-O bond of RCOO-*p*-C_6H_4X followed by decarbonylation of the acylnickel complex and decomposition of the alkylnickel complex: RCOO-*p*-$C_6H_4X + NiL_n \rightarrow RCONiL_nOC_6H_4X \rightarrow RNiL_nOC_6H_4X + CO$. The intermediate alkyl(phenoxo)nickel-type complex $NiCH_3(OC_6H_5)(bpy)$ was in fact isolated in the reaction of phenyl acetate with $Ni(cod)_2$ in the presence of 2,2′-bipyridine. The rate of the reaction is first order with respect to the concentration of the zerovalent nickel complex and the pseudo-first-order rate constant increases with the increase in the basicity of the phosphine ligand added and with the increase in the electron-withdrawing ability of X. On the basis of these results a mechanism involving a nucleophilic attack at the carbonyl carbon by nickel is proposed. The activation parameters for the reaction of $C_2H_5COOC_6H_5$ with the mixture of $Ni(cod)_2$ and PPh_3 are $\Delta H^{\ddagger} = 21 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -8.8 \pm 2.9$ eu.

Introduction

Although cleavage of an ester bond catalyzed by an alkali and acid has been extensively studied, activation and cleavage of the ester bond by a transition-metal complex in nonaqueous solvents are the subject of recent interest.[1-7] Some of the transition metal promoted cleavage reactions of the allyl-O bonds of allyl esters have been utilized for organic synthesis[6] and preparation of π-allyl complexes.[1,7]

In spite of the increasing interest concerning the transition metal promoted C-O bond cleavage of esters a detailed study of the reaction process has not been made. Previously we reported in a communication form the following two types of oxidative additions of esters to Ni(0) complexes and that the mode of the scission of the ester bond depends on the ester employed and the ligand coordinated to nickel:[8]

$$RCOOR' + NiL_n \rightarrow RCONiL_nOR' \text{ (type A)} \qquad (1)$$

$$RCOOR' + NiL_n \rightarrow RCOONiL_nR' \text{ (type B)} \qquad (2)$$

0002-7863/80/1502-3758$01.00/0

Table I. Products of the Reactions of Phenyl Carboxylates RCOO-*p*-C_6H_4X with Mixtures of $Ni(cod)_2$ and Ligand

expt	ester		ligand (L)	L/Ni	solvent (mL/mL of ester)	temp, °C	time, h	R(-H)	products (% yield/$Ni(cod)_2$)			
	R =	X =							*p*-XC_6H_4OH		Ni complex	others
1	C_2H_5	H	none		none	RT	24	sm	sm		Ni metal	
2	C_2H_5	H	PPh_3	1	none	54	12	40	50		$Ni(CO)L_3$ (sm)[a]	$(C_2H_5)_2CO$ (sm) COD isomers
3	C_2H_5	H	PPh_3	2	none	54	12	60	60		$Ni(CO)L_3$ (30)[a]	$(C_2H_5)_2CO$ (sm) COD isomers
4	C_2H_5	H	PPh_3	3	none	54	20	90	90		$Ni(CO)L_3$ (60)[a]	$(C_2H_5)_2CO$ (sm) COD isomers
5	C_2H_5	H	PPh_3	4	none	54	20	100	100		$Ni(CO)L_3$ (60)[a]	$(C_2H_5)_2CO$ (sm) COD isomers
6	C_2H_5	H	PPh_3	10	none	54	21	100	100		$Ni(CO)L_3$ (80)[a]	$(C_2H_5)_2CO$ (sm) COD isomers
7	C_2H_5	H	P(*p*-$C_6H_4CH_3)_3$	3	$CH_3COC_6H_5$ (10)	65	50	80	100		$Ni(CO)L_3$ (85)[b]	
8	C_2H_5	H	P(*p*-C_6H_4O-$CH_3)_3$	3	$CH_3COC_6H_5$ (10)	65	50	90	80		$Ni(CO)L_3$, *c*	
9	C_2H_5	H	PPh_2(*p*-C_6H_4-OCH_3),	3	$CH_3COC_6H_5$ (10)	65	50	80	85		$Ni(CO)L_3$ (76)[b]	
10	C_2H_5	H	PEt_3	2	mesitylene (3)	55	27	28	trace		$Ni(CO)_2L_2$ + $Ni(OC_6H_5)_2$, *d*	C_2H_6 (22)
11	C_2H_5	H	$P(OC_6H_5)_3$	2	none	65	6				no C-O bond cleavage proceeds	
12	C_2H_5	H	bpy	2.5	benzene (2.5)	65	24	13	trace		$Ni(CO)_mL_n$ + $Ni(OC_6H_5)_2L_n$, *d*	C_2H_6, 18
13	C_2H_5	H	bpy	1.2	THF (2.3)	60	3	8	14		$Ni(CO)_mL_n$ + $Ni(OC_6H_5)_2L_n$, *d*	C_2H_6, 42
14	C_2H_5	CH_3	PPh_3	3	none	70	8	60	60		$Ni(CO)L_3$ (60)[b]	
15	C_2H_5	OCH_3	PPh_3	3	none	70	8	70	80		$Ni(CO)L_3$ (90)[b]	
16	C_2H_5	CN	PPh_3	3	$CH_3COC_6H_5$ (5)	70	27	130	170		$Ni(CO)L_3$ + $Ni(CO)_2L_2$, *d*	
17	C_2H_5	H	$Ni(PPh_3)_4$		none	54	20	100	91		$Ni(CO)L_3$ (60)[b] + $Ni(C_2H_5COO)_2$ (sm)	
18	C_2H_5	H	Ni(CO)-$(PPh_3)_3$		none	60					no C-O cleavage proceeds	
19	*n*-C_3H_7	H	PPh_3	3	$CH_3COC_6H_5$ (10)	65	50	73	*c*		$Ni(CO)L_3$, *c*	
								CH_4	C_2H_6	ΣCH_3	Ni complex	others
20	CH_3	H	PPh_3	1.5	none	53	30	13	2	17	$Ni(CO)L_3$ (17)[a] + $Ni(OC_6H_5)_2$, *c*	anisole (sm)
21	CH_3	H	PPh_3	2	none	58	75	14	2	18	$Ni(CO)L_3$ (13)[a] + $Ni(OC_6H_5)_2$, *c*	anisole (sm)
22	CH_3	H	bpy	1.2	none	10	12	18	sm	18	$NiCH_3(OC_6H_5)L$ (20)[a] + $Ni(CO)_2L_2$, *c* + $Ni(OC_6H_5)_2$, *c*	
23	CH_3CO-OC_2H_5		PPh_3	2	none	50	2				C-O bond cleavage scarcely proceeds	

[a] Yields after recrystallization. sm = small amount. [b] Yields of unpurified complex. [c] Formation of the compound was confirmed by IR, NMR, and/or GLC, but the amount was not determined. [d] The yields were not determined owing to difficulties in separating the complexes from the mixture.

Of the two types of reactions the scission of the RCOO-R′ bond (type B) has been often observed in reactions between transition-metal complexes and esters[1-4,6,7] but only a few reports[5] have been made on the cleavage of the RCO-OR′ bond (type A) by the interaction with transition-metal complexes.

We now report details of type A cleavage reaction of phenyl carboxylates RCOO-*p*-C_6H_4X (R = CH_3, C_2H_5, *n*-C_3H_7; X = H, CH_3, OCH_3, CN) promoted by mixtures of bis(1,5-cyclooctadiene)nickel,$Ni(cod)_2$, and basic ligands such as tertiary phosphines and 2,2′-bipyridine.

Results and Discussion

Products, Stoichiometry, and Reaction Route. Table I summarizes products of the reactions of RCOO-*p*-C_6H_4X with $Ni(cod)_2$ in the absence or in the presence of ligands. In the absence of the ligand, $Ni(cod)_2$ is not stable in solutions containing esters and nickel metal deposits as a mirror with formation of only small amounts of alkanes (RH), olefins (R(-H)), and *p*-XC_6H_4OH. On the other hand, in the presence of the ligand the reaction proceeds smoothly under moderate conditions to afford products which are considered to be formed through oxidative addition of the esters to Ni.

Reactions of Phenyl Propionate with $Ni(cod)_2$ in the Presence of Triphenylphosphines. When phenyl propionate is employed as the ester and triphenylphosphine (PPh_3) is added as the ligand, the reaction affords C_2H_4, $Ni(CO)(PPh_3)_3$, and C_6H_5OH in about 1:1:1 ratio. The formation of these products indicates that both the C_2H_5CO-OC_6H_5 and C_2H_5-$COOC_6H_5$ bonds are cleaved in the reaction. No C-O bond cleavage of the ester occurred with the phosphine ligands such as PPh_3 and PEt_3 in the absence of $Ni(cod)_2$. A reasonable reaction pathway is the one involving the initial cleavage of the C_2H_5CO-OC_6H_5 bond followed by decarbonylation as shown in Scheme I.

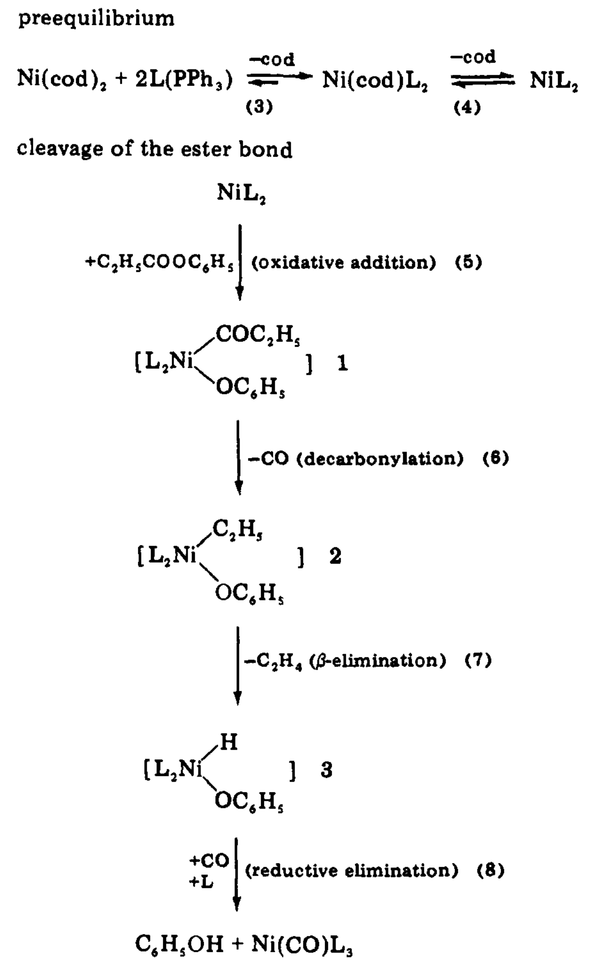
The total of the elemental reactions may be expressed

$$Ni(cod)_2 + 3PPh_3 + C_2H_5COOC_6H_5 \rightarrow Ni(CO)(PPh_3)_3 + C_2H_4 + C_6H_5OH + 2cod \quad (9)$$

The oxidative addition of the ester to yield the acyl(phenoxo)nickel complex **1** is somewhat analogous to the oxidative addition of an acyl halide to form an acylnickel complex which is further decarbonylated.[9b,d] The ensuing decarbonylation reaction of the acylnickel complex is considered to proceed smoothly as has been observed in the decarbonylation of isolated acylnickel complexes.[9a,c] The ethyl(phenoxo)nickel complex **2** thus formed is assumed to undergo β-elimination reaction to produce C_2H_4 and a hydrido(phenoxo)nickel complex **3**, from which phenol is reductively eliminated. Carbon monoxide formed by the decarbonylation reaction (6) may remain coordinated to Ni in **2** and **3** during the ensuing reactions (7) and (8) or may be liberated to be trapped by other zerovalent nickel species present in the reaction mixture. Carbon monoxide is eventually incorporated into a nickel carbonyl complex $Ni(CO)(PPh_3)_3$.

Concerning reaction 3, it is known that $Ni(cod)(PPh_3)_2$ can be isolated from a solution containing $Ni(cod)_2$ and PPh_3.[10] Actually the ^{31}P NMR spectrum of a 1:2 mixture of $Ni(cod)_2$ and PPh_3 shows a strong peak assignable to $Ni(cod)(PPh_3)_2$

Scheme I



at 43.6 ppm downfield from the external PPh_3 in benzene. Other zerovalent nickel species such as $Ni(cod)(PPh_3)$ and $Ni(PPh_3)_3$ are also present in small amounts as revealed by the ^{31}P NMR and they may participate in the oxidative addition of the ester in a similar manner as shown by reactions 4–8. In fact $Ni(PPh_3)_4$, which is known to be dissociated in solution to $Ni(PPh_3)_3$ and PPh_3, did participate in the oxidative addition as shown in Table I (expt 17).

The postulated mechanism and the stoichiometry of the reaction (eq 9) are supported by the following facts:

(a) Formation of diethyl ketone, which is considered to be formed by a coupling reaction between **1** and **2**, was observed in the reaction of $C_2H_5COOC_6H_5$ with $Ni(cod)_2$ and PPh_3.

(b) 1,5-Cyclooctadiene (COD) was isomerized to give a mixture of cyclooctadienes and bicyclooctenes (e.g., in expt 4 of Table I, 1,3-cyclooctadiene, 1,4-cyclooctadiene, COD, bicyclooctene-1, and bicyclooctene-2 were formed in a ratio of 7:20:43:1:29). The isomerization may be best explained by assuming the presence of a nickel hydride intermediate such as **3**. The COD isomerization in the present reaction proceeds at lower temperatures than that promoted by other transition-metal complexes.[11] The presence of the Ni–H species is supported also by the occurrence of ethylene dimerization when the reaction was carried out under high pressure (50 atm) of ethylene.

(c) When more than 3 mol of PPh_3 was used per mol of $Ni(cod)_2$, the yields of the products are determined by the amount of $Ni(cod)_2$, producing 1 mol of C_2H_4, 1 mol of C_6H_5OH, and 1 mol of $Ni(CO)(PPh_3)_3$. On the contrary, when the amount of PPh_3 was lessened, the extent of the reaction is restricted by the amount of PPh_3, and the yield of each product is reduced to about ⅓ mol per PPh_3 in agreement with the stoichiometry of the reaction (eq 9).

(d) In the reaction of $CH_3COOC_6H_5$ with $Ni(cod)_2$ in the presence of the 2,2′-bipyridine (bpy) ligand, a complex of type **2**, $NiCH_3(OC_6H_5)(bpy)$, can be isolated from the reaction mixture (expt 22). The isolated methyl(phenoxo)nickel complex was unequivocally characterized by comparison with the sample prepared by treatment of $Ni(CH_3)_2(bpy)$ with phenol.[12] Thus the intermediate formation of the alkyl(phenoxo)nickel type complexes in the reactions with the phenyl carboxylates is considered quite probable, although the attempts to isolate the ethyl(phenoxo)nickel analogue in the reaction of $Ni(cod)_2$, bipyridine, and phenyl propionate failed. The failure of isolation is probably due to the instability of $Ni(C_2H_5)(OC_6H_5)(bpy)$ in the presence of COD. The ethyl(phenoxo)nickel complex, $Ni(C_2H_5)(OC_6H_5)(bpy)$, prepared by treatment of $Ni(C_2H_5)_2(bpy)$ with phenol was in fact revealed to be unstable in the presence of COD to liberate ethane and ethylene, although the ethyl(phenoxo)nickel complex is considerably stable in organic solvents in the absence of olefins.

Reactions in the Presence of Other Phosphines or bpy. Addition of the other triarylphosphines in the reaction of $C_2H_5COO_6H_5$ with $Ni(cod)_2$ gives similar products as those obtained by addition of PPh_3. When a more basic triethylphosphine was used in the reaction of $C_2H_5COOC_6H_5$ with $Ni(cod)_2$ (expt 10), a 1:1 mixture of ethylene and ethane was evolved with formation of $Ni(OC_6H_5)_2$ and $Ni(CO)_2(PEt_3)_2$. The result suggests that the intermediate PEt_3-coordinated ethylnickel phenoxide does not collapse through a route involving β-elimination followed by reductive elimination of phenol but it decomposes through a disproportionation reaction liberating ethylene and ethane with formation of $Ni(OC_6H_5)_2$ as shown below:

$$2C_2H_5Ni(PEt_3)_2OC_6H_5 \xrightarrow{+2CO} C_2H_4 + C_2H_6 + Ni(CO)_2(PEt_3)_2 + Ni(OC_6H_5)_2 \quad (10)$$

That the molar ratio of C_2H_4 to C_2H_6 was unity supports the view that C_2H_4 and C_2H_6 were produced by the disproportionation of the ethyl group.

Addition of $P(OC_6H_5)_3$, which has a weaker basicity than the tertiary phosphines, did not cause the C–O bond cleavage (expt 11).

When bpy was added in the reaction of $C_2H_5COOC_6H_5$ with $Ni(cod)_2$ in benzene (expt 12), a ca. 1:1 mixture of C_2H_4 and C_2H_6 was evolved with formation of $Ni(OC_6H_5)_2L_n$ and $Ni(CO)_mL_n$ as described previously. The result suggests that the intermediate ethylnickel species collapses through a similar disproportionation reaction to that represented by eq 10. When the same reaction was carried out in THF (expt 13), a hydrogen-donating solvent, the proportion of ethane in the ethane–ethylene mixture increased considerably, suggesting that a part of the ethylnickel intermediate in THF collapses through hydrogen abstraction from the solvent to produce C_2H_6.

Reactions of Other Aryl Propionates. On employing an ester having CH_3 or OCH_3 substituent at the phenyl ring, similar products as those obtained by employing $C_2H_5COOC_6H_5$ were produced (expt 14 and 15). When the ester bond is strongly activated by a cyano group at the phenyl ring (expt 16), the reaction gives a dicarbonylnickel complex, $Ni(CO)_2(PPh_3)_2$, with evolution of more than 1 mol of C_2H_4 per $Ni(cod)_2$, presumably through further oxidative addition of the ester to $Ni(CO)(PPh_3)_3$, which has no reactivity toward phenyl propionate without the activating cyano group (expt 18):

$$C_2H_5COO\text{-}p\text{-}C_6H_4CN + Ni(CO)(PPh_3)_3 \rightarrow C_2H_4 + p\text{-}HOC_6H_4CN + Ni(CO)_2(PPh_3)_2 + PPh_3 \quad (11)$$

The reaction of phenyl butyrate with the mixture of $Ni(cod)_2$ and PPh_3 gives similar results to those of the reaction of phenyl propionate, yielding propylene, phenol, and $Ni(CO)(PPh_3)_3$.

Reaction of Phenyl Acetate. The products of the reaction of $CH_3COOC_6H_5$ in the presence of PPh_3 can be elucidated by a similar reaction mechanism as that proposed for the reaction of $C_2H_5COOC_6H_5$. Formation of $Ni(CH_3)(OC_6H_5)(bpy)$ in the reaction of phenyl acetate in the presence of 2,2′-bipyridine is consistent with the postulated mechanism involving the oxidative addition of $RCOOC_6H_5$ to Ni and ensuing decarbonylation of the acetylnickel species. The rest of the reaction pathway, however, takes a somewhat different route from that of the reaction of the propionate by the difference in nature between the ethyl and methylnickel intermediate, the latter having no abstractable β hydrogens and decomposing with evolution of methane and ethane. Formation of $Ni(OC_6H_5)_2$ suggests that a disproportionation reaction took place at some stage of the reaction. A similar disproportionation reaction of a methylnickel complex with an acac ligand has been observed.[13] The ratio between $Ni(CO)(PPh_3)_3$ and the sum of the methyl groups, ΣCH_3, detected as methane and ethane in Table I roughly agrees with the stoichiometry of the following reaction:

$$3Ni(cod)_2 + 2CH_3COOC_6H_5 + 6PPh_3 \rightarrow 2Ni(CO)(PPh_3)_3 + 2\text{“}CH_3\text{”} + Ni(OC_6H_5)_2 \quad (12)$$

The formation of small amounts of anisole in expt 20 and 21 renders additional evidence to the postulated formation of the methyl(phenoxo)nickel species in the reactions.

In contrast to the isomerization of COD in the reaction of $C_2H_5COOC_6H_5$, COD is not isomerized in the reaction of $CH_3COOC_6H_5$, presumably owing to the poor catalytic activity of the methylnickel intermediate for the isomerization. The oxidative addition of $CH_3COOC_6H_5$ proceeded at a considerably slower rate than the oxidative addition of $C_2H_5COOC_6H_5$ and the yields of the products were lower.

Alkyl carboxylates such as $CH_3COOC_2H_5$ scarcely undergo the oxidative addition to nickel (expt 23); only trace amounts of gases originated from the esters were evolved in the reactions of the esters at elevated temperatures.

Reversibility of the Oxidative Addition. Although the isolation of the postulated acyl(phenoxo)nickel(II) intermediate **1** in the ester cleavage reactions was not feasible, the acyl(phenoxo)nickel(II) type complexes can be prepared through an independent route by using alkyl(p-cyanophenoxo)(2,2′-bipyridine)nickel(II) ($NiR(O\text{-}p\text{-}C_6H_4CN)(bpy)$) and CO as the starting materials. The reaction of $NiR(O\text{-}p\text{-}C_6H_4CN)(bpy)$ and CO in a 1:1 ratio at −78 °C affords the acyl(phenoxo)nickel(II) type complexes, **4a** and **4b**, in good yield:[12]

$$\underset{1}{NiR(O\text{-}p\text{-}C_6H_4CN)(bpy)} + \underset{1}{CO} \xrightarrow{-78\ ^\circ C} \begin{matrix} Ni(COR)(O\text{-}p\text{-}C_6H_4CN)(bpy) \\ R = C_2H_5\ (\mathbf{4a}),\ CH_3\ (\mathbf{4b}) \end{matrix} \quad (13)$$

The complexes **4a** and **4b** are stable in solution at room temperature, but addition of excess CO causes reductive elimination of $RCOO\text{-}p\text{-}C_6H_4CN$ from **4** with formation of $Ni(CO)_2(bpy)$, indicating that the coordination of excess CO to **4** induces the reductive coupling of acyl and p-cyanophenoxo groups on **4**. The reductive elimination of ester from the isolated acyl(p-cyanophenoxo)nickel complexes was promoted also by interaction of various π acids such as maleic anhydride (MAH) and ethyl methacrylate. When **4a** and **4b** were treated with excess MAH in THF at room temperature for 1 day, p-cyanophenyl esters $C_2H_5COOC_6H_4CN$ (0.62 mol/Ni) and $CH_3COOC_6H_4CN$ (0.70 mol/Ni), respectively, were produced with formation of $Ni(MAH)_2(bpy)$[14] (0.77–0.90 mol/Ni), the fact indicating that the Ni–COR and Ni–OC_6H_4CN bonds of **4** are activated by the coordination of MAH to cause the reductive elimination. Addition of a somewhat weaker π acid, ethyl methacrylate, also causes the reductive elimination with a lower yield. A similar effect of an olefin to induce a reductive coupling of dialkylnickel complexes releasing R–R and giving $Ni(olefin)_n(bpy)$ has been reported.[14] These results clearly indicate that the oxidative addition of ester to Ni is a reversible reaction.

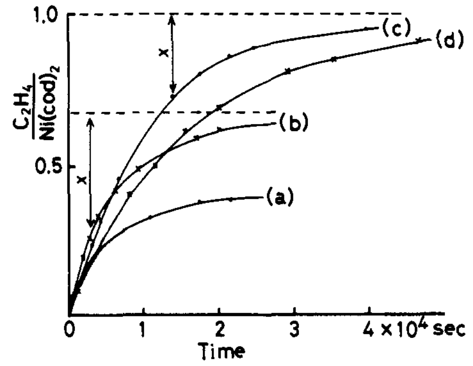


Figure 1. Time course of the evolution of C_2H_4 in the reaction of $C_2H_5COOC_6H_5$ with $Ni(cod)_2$ in the presence of (a) 1, (b) 2, (c) 3, and (d) 4 mol of PPh_3 per $Ni(cod)_2$, temperature 54 °C.

Although the complexes **4a** and **4b** are stable in solutions, they are readily decarbonylated in the presence of Ni(0) complexes such as $Ni(PPh_3)_4$ to afford $NiR(O\text{-}p\text{-}C_6H_4CN)(bpy)$ and Ni–CO complex(es) (e.g., $Ni(CO)(PPh_3)_3$). A similar decarbonylation of the acetylnickel complex on interaction with $Ni(PMe_3)_4$ has been observed.[9a] This explains why the initial oxidative addition products, $Ni(COR)(O\text{-}p\text{-}C_6H_4CN)$, were not isolated but only the decarbonylated products were obtained. Reactions of other alkyl(phenoxo)nickel type complexes $NiR(OR')L_2$ which have no electron-withdrawing substituent at the phenyl ring with CO afforded the corresponding ester RCOOR′, without yielding the acyl(phenoxo)nickel type complexes.

Oxidative Addition of $RCOOC_6H_5$ to Ni(II) Complexes. Although the interaction of $RCOOC_6H_5$ with electron-deficient Ni(II) complexes such as $NiBr_2(PPh_3)_2$ and $NiCl_2(bpy)$ does not promote C–O bond cleavage of $RCOOC_6H_5$ even at 100 °C, the C–O bond is cleaved at room temperature on interaction with dialkylnickel(II) complexes which are formally divalent but more electron rich than halides. For example, the reaction of $Ni(CH_3)_2(PEt_3)_2$ with $RCOOC_6H_5$ ($R = C_2H_5$, C_6H_5) at room temperature affords 9–22 mol % $RCOCH_3$ and 3–20 mol % acetone per complex with formation of $Ni(CH_3)(OC_6H_5)(PEt_3)_2$. The formation of acetone suggests the scrambling of CO liberated from the COR ligand on nickel.

Kinetics. Figure 1 shows the time course of the evolution of C_2H_4 in the reaction of $C_2H_5COOC_6H_5$ with $Ni(cod)_2$ in the presence of PPh_3. Since a good agreement between the amount of C_2H_4 evolved and that of $C_2H_5COOC_6H_5$ consumed is observed at any time of the reaction, the amount of ethylene evolved can be taken as a good measure to follow the extent of the reaction. It is seen in Figure 1 that the amount of C_2H_4 evolved increases with time approaching a limiting value, which corresponds to 1 mol per $Ni(cod)_2$ in the presence of more than 3 mol of PPh_3 per $Ni(cod)_2$ and about 1/3 mol per PPh_3 in the presence of a less amount of PPh_3 in accordance with the stoichiometry (eq 9).

Plotting of log x in Figure 1 against time gives straight lines (Figure 2), demonstrating that the rate of the reaction is proportional to the amount of an intact nickel(0)–phosphine complex such as $Ni(cod)(PPh_3)_2$. The pseudo-first-order rate constant k is determined by the slope of the straight line and the k values under various conditions are summarized in Table II. The dependence of the reaction conditions on the rate constant k is as follows.

Table II. Pseudo-First-Order Rate Constant *k* of the Reaction of RCOO-*p*-C_6H_4X with $Ni(cod)_2$ in the Presence of Phosphine Ligand

no.	ester	phosphine (PR_3)	PR_3/Ni	temp, °C	solvent	[ester], M	$k \times 10^4$, s^{-1}
1	$C_2H_5COOC_6H_5$	PPh_3	1	54	none	7.0	1.1
2	$C_2H_5COOC_6H_5$	PPh_3	2	54	none	7.0	1.3
3	$C_2H_5COOC_6H_5$	PPh_3	3	54	none	7.0	0.8
4	$C_2H_5COOC_6H_5$	PPh_3	4	54	none	7.0	0.6
5	$C_2H_5COOC_6H_5$	PPh_3	10	54	none	7.0	0.6
6	$C_2H_5COOC_6H_5$	PPh_3	3	65	none	7.0	1.2
7	$C_2H_5COOC_6H_5$	PPh_3	3	65	$CH_3COC_6H_5$	0.64	0.10
8	$C_2H_5COOC_6H_5$	PPh_3	3	70	none	7.0	2.8
9	$C_2H_5COOC_6H_5$	PPh_3	3	75	none	7.0	4.0
10	$C_2H_5COOC_6H_5$	PPh_3	3	80	$(C_6H_5)_2CH_2$	1.6	3.6
11	$C_2H_5COOC_6H_5$	PPh_3	3	80	$(C_6H_5)_2CH_2$	3.5	4.5
12	$C_2H_5COOC_6H_5$	PPh_3	3	80	$(C_6H_5)_2CH_2$	5.3	6.4
13	$C_2H_5COOC_6H_5$	PPh_3	3	80	none	7.0	6.8
14	$C_2H_5COOC_6H_5$	PPh_3	3	85	none	7.0	11
15	$C_2H_5COOC_6H_5$	$Ni(PPh_3)_4$		85	none	7.0	14
16	$C_2H_5COOC_6H_5$	$PPh_2(p\text{-}C_6H_4OCH_3)$	3	65	$CH_3COC_6H_5$	0.64	0.12
17	$C_2H_5COOC_6H_5$	$P(p\text{-}C_6H_4CH_3)_3$	3	65	$CH_3COC_6H_5$	0.64	0.22
18	$C_2H_5COOC_6H_5$	$P(p\text{-}C_6H_4OCH_3)_3$	3	65	$CH_3COC_6H_5$	0.64	0.70
19	$C_2H_5COOC_6H_5$	PEt_3	2	30	none	7.0	0.70
20	$C_2H_5COOC_6H_5$	PEt_3	3	55	mesitylene	1.8	0.82
21	$C_2H_5COO\text{-}p\text{-}C_6H_4OCH_3$	PPh_3	3	70	none	5.9	1.6
22	$C_2H_5COO\text{-}p\text{-}C_6H_4CH_3$	PPh_3	3	70	none	6.4	2.2
23	$C_2H_5COO\text{-}p\text{-}C_6H_4CN$	PPh_3	3	70	$CH_3COC_6H_5$	1.0	(17)[a]

[a] The reaction of C_2H_5COO-*p*-C_6H_4CN did not obey the first-order rate law and the value given was computed from the initial rate of the reaction by assuming $k = (d[C_2H_4]/dt)_{t=0}/[Ni(cod)_2]$.

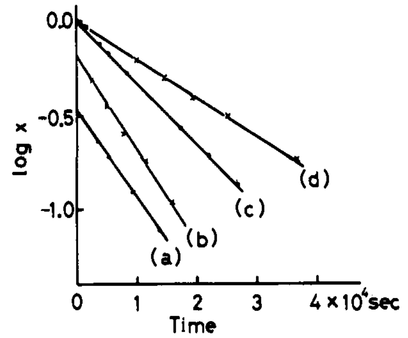


Figure 2. First-order plot of the data in Figure 1. The letters designating the straight lines refer to the letters of the curves in Figure 1.

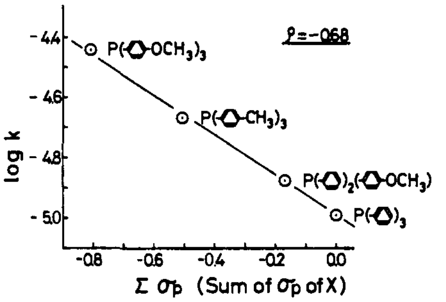


Figure 3. Plot of the logarithm of the pseudo-first-order rate constant *k* against the sum of σ_p's of the para substituents of $P(p\text{-}C_6H_4Y_1)(p\text{-}C_6H_4Y_2)(p\text{-}C_6H_4Y_3)$.

Amount of the Phosphine Ligand Added. Although the final amount of C_2H_4 evolved increases with increase in the amount of PPh_3 added, the rate constant reaches a maximum at $PPh_3/Ni(cod)_2 = 2$ and then decreases, indicating that coordination of PPh_3 to nickel is essential for the reaction to proceed but the presence of too much PPh_3 interferes with the interaction of the ester with nickel. That the rate of reaction reaches a maximum at $PPh_3/Ni(cod)_2 = 2$ is consistent with our assumption that $Ni(cod)(PPh_3)_2$ is one of the most active species (eq 3-8).

Concentration of Ester. The pseudo-first-order rate constant *k* increases with increase in the concentration of phenyl propionate (no. 10-13 in Table II). A plot of 1/*k* vs. the reciprocal of the phenyl propionate concentration is roughly linear, suggesting that the reaction proceeds through a Michaelis-Menten-type reaction mechanism with a coordination equilibrium of the ester to nickel.

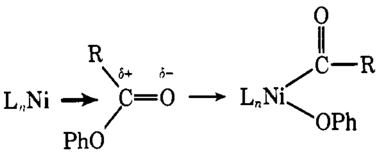
Basicity of the Phosphine Ligand. Figure 3 shows a plot of the logarithms of the pseudo-first-order rate constants *k* against the sum of the Hammett σ_p's of the para substituents in $P(p\text{-}C_6H_4Y_1)(p\text{-}C_6H_4Y_2)(p\text{-}C_6H_4Y_3)$ ($\Sigma\sigma_p = \sigma_p(Y_1) + \sigma_p(Y_2) + \sigma_p(Y_3)$). The plot gives a straight line with a slope of -0.68, the negative value showing that the increase in the nucleophilicity of nickel by coordination of more basic ligands enhances the reactivity of the nickel complex toward ester. Coordination of the more basic ligands such as PEt_3 to Ni increases the reactivity of the nickel complex and the oxidative addition proceeds in this case at a considerable rate even at 0 °C. Similar results are observed on addition of other trialkylphosphines. The pseudo-first-order rate constant obtained at 30 °C in the presence of PEt_3 is comparable to that obtained at 54 °C with PPh_3.

Substituent at the Phenyl Ring of Phenyl Propionate. It is seen in Table II that the substitution of the para hydrogen of the phenyl ring in phenyl propionate by an electron-withdrawing group such as CN enhances the reactivity of the ester, whereas the substitution by an electron-donating group such as OCH_3 decreases the reactivity. This trend is consistent with the assumption that the reaction proceeds through a nucleophilic attack of nickel at the carbonyl carbon of the ester. The Hammett plot of the logarithm of the rate constant against σ_p of the substituent X gives a roughly linear relationship with a ρ value of $+1.5$, the value being comparable to the reported ρ values ($+0.76$ to $+2.5$)[15] for the hydrolysis of esters by OH^- under various conditions. The hydrolysis of esters by acid is known to give ρ values of an entirely different range (-0.13 to $+0.03$).[15] The low reactivity of alkyl carboxylates (no. 23 in Table I) is attributable to a feeble electron-withdrawing ability of the alkyl group.

Activation Energy. Apparent activation energy for the reaction of $C_2H_5COO_6H_5$ with $Ni(cod)_2$ in the presence of 3 mol of PPh_3 per $Ni(cod)_2$ has been computed as 22 ± 2 kcal/mol from the temperature dependence of the rate constant. The activation parameters are $\Delta H^{\ddagger} = 21 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -8.8 \pm 2.9$ eu. The activation energy is somewhat larger than reported activation energies (10–19 kcal/mol)[16] for the hydrolysis of esters by OH^-.

Conclusion and Scope

The present study has clearly demonstrated that the RCO-OPh bond in carboxylic esters can be selectively cleaved under mild conditions and the reaction proceeds through an oxidative addition mechanism triggered by a nucleophilic attack of an electron-rich nickel complex at the carbonyl group in the ester:



(13)

Thus, the present nickel-promoted cleavage of the ester bond bears some resemblance to the hydrolysis of esters with alkali proceeding through a nucleophilic attack of OH^- at the carbonyl carbon However, the poor reactivity of aliphatic esters such as ethyl acetate together with the high reactivities of allyl and vinyl carboxylates[8] as well as allyl alcohol and allyl ethers[17] toward Ni(0) complexes (type B cleavage) may be taken as an indication that π electrons of the benzene ring in phenyl carboxylates are also interacting with nickel to assist the attack at the carbonyl group leading to the C-O bond cleavage.

The ester cleavage reported here is reminiscent of decarbonylation of aldehydes and acyl halides promoted by Rh complexes[18] which have found some synthetic utility. In the cleavage process of phenyl propionate, the involvement of EtCO-OPh bond cleavage, decarbonylation and β-hydrogen abstraction accompanied by reductive elimination of PhOH from a PhO-Ni-H species in the reaction sequence has been indicated with experimental support. The result together with the realization of the reverse process, i.e., a stepwise CO insertion into the R-Ni bond of R-Ni-OPh-type complexes and reductive elimination of ester from the RCO-Ni-OPh species promoted by π acids, suggests the potential applicability of the present finding. Design of synthetic processes combining the oxidative addition and reductive elimination processes coupled with insertion and/or deinsertion processes involving other substrates such as olefins and CO by a suitable choice of transition metals and ligands is conceivable. A process utilizing the decarbonylation of esters prompted by our previous communication[8] has already been realized using a Ni(0) complex[5c] and future study will reveal the further development of processes utilizing the transition metal promoted facile C-O bond cleavage reactions.

Experimental Section

General Procedures and Materials. Manipulation of complexes and the reactions were carried out under deoxygenated nitrogen or argon or under vacuum. $Ni(cod)_2$ was purchased from Merck Co., Ltd., and recrystallized. Esters were purified by repeated distillation until their gas chromatograms show no significant peaks of contaminants. Tertiary phosphine ligands and bpy were used as purchased or synthesized by the methods given in the literature.[19] Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen.

Reaction of Esters with Zerovalent Nickel Complexes (Refer to Table I). Experiments 2–6. Phenyl propionate (2.5 mL, 18 mmol) was added to a Schlenk-type flask containing 130 mg (0.47 mmol) of $Ni(cod)_2$ and 370 mg (1.4 mmol, $PPh_3/Ni = 3$) of PPh_3 and the mixture was stirred at 54 °C after evacuation of a gas in the flask. After 20 h evolution of 0.42 mmol (volumetry) of C_2H_4 was observed. Analysis of the liquid phase by GLC showed formation of 0.42 mmol of C_6H_5OH and a small amount of diethyl ketone. GLC analysis revealed also that the 1,5-cyclooctadiene (COD) ligand was isomerized to give a mixture of 1,3-cyclooctadiene, 1,4-cyclooctadiene, COD, bicyclooctene-1, and bicyclooctene-2 (7:20:43:1:29). Removing volatile material under vacuum yielded a light yellow solid whose IR spectrum is almost identical with that of the known $Ni(CO)(PPh_3)_3$,[20] showing a sharp ν(C═O) band at 1926 cm^{-1}. Recrystallization from THF-hexane afforded 240 mg (0.28 mmol) of $Ni(CO)(PPh_3)_3$. Analytical data of the complex agreed with the structure. The reactions in the presence of 1, 2, 4, or 10 mol of $PPh_3/Ni(cod)_2$ were carried out in similar manners. Formation of a nickel mirror after a prolonged reaction was observed when the reaction was carried out in the presence of less than 3 mol of PPh_3 per $Ni(cod)_2$.

Experiments 7–9. Experiments were carried out in similar manners to expt 2-6. Monocarbonyl complexes of type $Ni(CO)L_3$ produced were identified by a single strong ν(C═O) band in the IR spectrum of the solid recovered from the reaction mixture. ν(C═O): $Ni(CO)(P(p\text{-}C_6H_5CH_3)_3)_3$ (brown), 1900 cm^{-1}; $Ni(CO)(P(p\text{-}C_6H_5OCH_3)_3)_3$ (pale brown), 1905 cm^{-1}; $Ni(CO)(P(C_6H_5)_2(p\text{-}C_6H_5OCH_3))_3$ (yellow), 1910 cm^{-1}.

Experiment 10. Mesitylene (3 mL) was added to a mixture of $Ni(cod)_2$ (280 mg, 1.0 mmol), PEt_3 (0.22 mL, 2.0 mmol), and $C_2H_5COOC_6H_5$ (1.0 mL, 6.0 mmol). Stirring the reaction system for 27 h at 55 °C gave 0.28 mmol of C_2H_4 and 0.22 mmol of C_2H_6 (volumetry and GLC). The IR spectrum of the recovered solid showed ν(C═O) bands of $Ni(CO)_2(PEt_3)_2$[21] at 1980 and 1920 cm^{-1} and a ν(C—O) band at 1270 cm^{-1} which is characteristic of nickel phenoxides.

Experiment 11. Phenyl propionate (5 mL) was added to a Schlenk-type flask containing 140 mg (0.52 mmol) of $Ni(cod)_2$ and 330 mg (1.1 mmol) of $P(OC_6H_5)_3$. Stirring of the mixture at 65 °C for 6 h gave no indication of the oxidative addition of $C_2H_5COOC_6H_5$ to nickel.

Experiments 12 and 13. Tetrahydrofuran (8 mL) was added to a mixture of $Ni(cod)_2$ (1.46 g, 5.37 mmol), bpy (1.00 g, 6.40 mmol), and $C_2H_5COOC_6H_5$ (3.0 mL, 18 mmol). Stirring the reaction system for 3 h at 60 °C yielded a red solution and a black precipitate with evolution of C_2H_4 (0.42 mmol) and C_2H_6 (2.28 mmol). Separation and cooling of the red solution gave red prisms of $Ni(CO)_2(bpy)$ (0.20 g). The IR spectrum of the black precipitate showed absorption bands of nickel carbonyl complex(es) at 1970 (w) and 1830 (s) cm^{-1} and ν(C-O) at 1265 cm^{-1} which is characteristic of nickel phenoxide. Experiment 12 was carried out in a similar manner.

Experiments 14–19 were carried out in similar manners to expt 2-6.

Experiments 20 and 21. Phenyl acetate (7.0 mL, 63 mmol) was added to a Schlenk-type flask containing 1.3 g (4.7 mmol) of $Ni(cod)_2$ and 1.8 g (7.1 mmol) of PPh_3. Stirring the mixture at 50–55 °C for 30 h gave 0.63 mmol of CH_4 and 0.09 mmol of C_2H_6 (volumetry and GLC). Cooling down the reaction mixture to room temperature yielded a yellow precipitate, whose recrystallization from THF-hexane gave 700 mg (0.80 mmol, 17%/$Ni(cod)_2$) of $Ni(CO)(PPh_3)_3$. GLC analysis of the liquid phase revealed formation of a small amount of anisole. Addition of *n*-hexane to the solution, after removal of the precipitate, afforded a light brown solid. The following spectral and analytical data of the light brown solid indicates that it is $Ni(OC_6H_5)_2$: (1) The IR spectrum showed a ν(C-O) bond of phenoxo group at 1250 cm^{-1} and many bands characteristic of a phenyl ring. (2) The reaction with $(C_2H_5CO_2)O$ gave a calculated amount of $C_2H_5COOC_6H_5$ according to the following stoichiometry: $Ni(OC_6H_5)_2 + 2(C_2H_5CO)_2O \rightarrow Ni(C_2H_5COO)_2 + 2C_2H_5COOC_6H_5$.

Experiment 22. Phenyl acetate (1.0 mL, 9.0 mmol) was added to a mixture of 410 mg (1.5 mmol) of $Ni(cod)_2$ and 280 mg(1.8 mmol) of bpy. After the gas was evacuated in the reaction vessel, the mixture was stirred at 10 °C for 12 h to yield 0.22 mmol of CH_4 and 120 mg (0.36 mmol) of deep red $NiCH_3(OC_6H_5)(bpy)$, which was identified by comparing its IR spectrum with that of an authentic sample prepared by a 1:1 reaction of $Ni(CH_3)_2(bpy)$ with C_6H_5OH.[12]

Experiment 23. The reaction of $CH_3COOC_2H_5$ (3 mL) with a mixture of $Ni(cod)_2$ (420 mg, 1.5 mmol) and PPh_3 (810 mg, 3.0 mmol) at 70 °C gave no indication of the occurrence of the C-O bond cleavage. A mixture of zerovalent nickel species (mainly $Ni(cod)(PPh_3)_2$) was recovered from the reaction mixture.

Dimerization of C_2H_4 by Using a $Ni(cod)_2$-PPh_3-$C_2H_5COOC_6H_5$ System. Ethylene (50 atm) was introduced to a 100-mL autoclave containing $Ni(cod)_2$ (590 mg, 2.1 mmol), PPh_3 (1.1 g, 4.2 mmol),

$C_2H_5COOC_6H_5$ (5 mL), and toluene (14 mL). About 10% of C_2H_4 was consumed after the solution was stirred for 6 h. GLC analysis showed the formation of 1-butene.

Kinetic Studies. A 20-ml Schlenk tube containing $Ni(cod)_2$, ligand, aryl propionate, and solvent was connected to a vacuum line equipped with a mercury manometer and the system was evacuated. The Schlenk tube was surrounded by thermostated water controlled to ±0.5 °C. The reaction mixture was stirred by a magnetic stirrer and the rate of reaction was determined by measuring the volume of C_2H_4 evolved with time. When the concentration of ester was smaller than 0.5 M, the amount of C_2H_4 evolved became considerably smaller than 1 mol/$Ni(cod)_2$. This may be at least partly due to the trapping of the evolved C_2H_4 by nickel in the absence of enough of the ester and the data for the concentration range were omitted.

Spectral Measurement and Analysis. IR spectra were recorded on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS-100 spectrometer, and ^{31}P NMR spectra on a JEOL Model JNM-PFT-PS-100 Fourier transform spectrometer. Microanalysis of C, H, and N was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. The analyses of gaseous and liquid products were carried out with a Shimadzu GC-3BT or GC-6A gas chromatograph.

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The 147-nm Photolysis of Disilane[1]

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Received August 30, 1979

Abstract: The photodecomposition of Si_2H_6 at 147 nm results in the formation of H_2, SiH_4, Si_3H_8, Si_4H_{10}, Si_5H_{12}, and a solid film of amorphous silicon hydride (a-Si:H). Three primary processes are proposed to account for the results, namely, (a) $Si_2H_6 + h\nu \rightarrow SiH_2 + SiH_3 + H$ ($\phi_a = 0.61$); (b) $Si_2H_6 + h\nu \rightarrow SiH_3SiH + 2H$ ($\phi_b = 0.18$); (c) $Si_2H_6 + h\nu \rightarrow Si_2H_5 + H$ ($\phi_c = 0.21$). The overall quantum yields depend on the pressure but at 1 Torr partial pressure of Si_2H_6 are $\Phi(-Si_2H_6) = 4.3 \pm 0.2$, $\Phi(SiH_4) = 1.2 \pm 0.4$, $\Phi(Si_3H_8) = 0.91 \pm 0.08$, $\Phi(Si_4H_{10}) = 0.62 \pm 0.03$, $\Phi(Si, wall) = 2.2$. Quantum yields for H_2 formation were not measured. A mechanism is proposed which is shown to be in accord with the experimental facts.

Introduction

A substantial amount of kinetic and mechanistic information concerning the gas-phase reactions of silicon hydride radicals has been gained through the photolysis and photosensitized decomposition of various silanes. Monovalent silyl radicals are known to undergo combination and disproportionation reactions[2-8] and are effectively intercepted by common free-radical scavengers such as nitric oxide[5,6] and olefins.[9,10] Divalent silylene radicals insert readily into Si–H bonds of the substrate molecule to yield higher silanes,[11-15] but are apparently less reactive toward olefins[16] and are unreactive toward nitric oxide.[13]

The direct photochemical decompositions of silane,[15] methylsilane,[12,13] and dimethylsilane[14] at 147 nm are characterized by the favored production of divalent silylene radicals in the primary step. The $Hg(^3P_1)$-photosensitized decompositions of monosilane,[4-7,9] disilane,[3] and the methylsilanes[5] occur predominantly through the formation and subsequent reaction of monovalent silyl radicals.

The direct photolysis of Si_2H_6 has not previously been reported. As part of a general research program concerned with the development of silicon hydride free-radical chemistry, we have studied the photodecomposition of Si_2H_6 at 147 nm. This paper is a report of our results.

Experimental Section

The photolyses were carried out in a 38-cm^3 cylindrical stainless steel cell fitted with a lithium fluoride window and coupled via a

0002-7863/80/1502-3764$01.00/0