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REACTIONS OF LITHIUM WITH BENZALDEHYDE IN SOLUTION

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Benzaldehyde in THF reacts with lithium metal to give the expected reduction product, benzyl alcohol, plus benzoin and benzyl as minor products. The kinetics of the overall reaction as well as the partial rate coefficients of the several steps have been determined under various reaction conditions. It was found that adsorption on the surface and electron transfer from the lithium to benzaldehyde are the slow steps. The experimental results show interesting surface effects, and evidence for significant radical intermediates, which were characterized by their epr spectra and trapping experiments, results useful to gain insight into the mechanisms of these and other related reactions. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

There is increasing interest in the study of the mechanisms by which reactions with alkali and alkaline earth metals occur, from both fundamental[1–3] and applied points of view.[4, 5] The reduction of substituted amides with sodium[6] and the mechanism of formation of Grignard reagents[7] are just two examples related to the present work. Analogously, the well known Fisher–Tropsch process, for the industrial production of hydrocarbons from synthesis gas,[8] is based on the catalytic reductive coupling of CO, using an organometallic complex in which the metal is usually in a low valence state. The nature of the reactions that occur at the catalyst surface is a matter of intense research at present.[7–10]

We have recently provided substantial evidence that the first step of the complex mechanism of the solution reaction of phenyllithium with CO is electron transfer from PhLi to CO.[11] This paper reports a mechanistic study of the reduction of benzaldehyde by lithium metal. Evidence for a common radical intermediate for both reactions is presented.

RESULTS AND DISCUSSION

Reaction products and kinetics

Taking into account the solvent effects observed in the reactions of organolithium compounds,[10, 11] several solvents were examined in preliminary studies of this reaction. THF was selected as the most appropriate. The reactions of benzaldehyde, **1**, with lithium were carried out at several temperatures within the range 30–60 °C, for different reaction times, and the products were isolated and characterized by conventional techniques. As expected, the main reaction product is benzyl alcohol, **2**, but determinations of minor products [e.g. benzoin, **3**, and benzil, **4**; equation (1)] proved to be mechanistically significant. This mechanism is also a possible model for other reactions.

$$\underset{\mathbf{1}}{\mathrm{PhCHO}} + \mathrm{Li} \longrightarrow \underset{\mathbf{2}}{\mathrm{PhCH_2OH}} + \underset{\mathbf{3}}{\mathrm{PhCOCHOH\,Ph}} + \underset{\mathbf{4}}{\mathrm{PhCOCOPh}} \tag{1}$$

The rate of disappearance of reactant **1**, as well as the rate of appearance of the three products shown in equation (1), were followed at several temperatures by GC analysis of the reaction mixture at different time intervals. It was found that the reaction is sensitive to the reactant concentration, to the amount and overall area of the lithium metal and to the temperature. The reaction was quenched with a saturated solution of ammonium chloride and/or with acetic anhydride. In the latter case, the corresponding acetates of products **2** and **3** were isolated and the mass balance was

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Table 1. Reaction of benzaldehyde, **1**, with lithium in THF at 52.5 °C[a]

Time	Concentration (10^{-2} M)				**1**		
					Conversion	Recovered (%)	
(min)	[**1**]	[**2**]	[**3**]	[**4**]	(%)	$[\mathbf{1}]_{\mathrm{soln}}$	$[\mathbf{1}]_{\mathrm{adsorbed}}$
1	22.4	0.16	0.05	0.04	1	93	6
6	15.8	3.9	1.0	0.4	28	66	6
9	10.4	4.4	0.8	0.4	28	43	29
16	6.6	10.1	1.2	0.6	57	28	15
21	4.1	12.4	1.2	0.7	68	17	15
32	1.7	16.9	1.4	0.7	88	7	5
40	0.79	16.3	1.5	0.6	86	3	11
55	0.48	17.9	1.5	0.6	92	2	6

[a] $[\mathbf{1}]_0 = 0.24$ M; [Li] = 2.4 M; when quenching with acetic anhydride the corresponding acetates were isolated.

improved, probably owing to the lower solubilities of the products in that medium. In spite of being a complex heterogeneous reaction, conditions were found that gave highly reproducible results in the product distribution as well as in the kinetics, within reasonable experimental error.

The data describing a typical kinetic run are shown in Table 1 for the reaction carried out at 52·5 °C. While the concentration of **1** decreases steadily, there may be a slight lag (short induction period) for the formation of **2**. The rates of appearance of products **3** and **4** are much less and their low yields preclude judgements of the exact form of their appearance curves. The amounts of **1** on the lithium surface were also determined and are given in the last column of Table 1 as $[\mathbf{1}]_{\mathrm{adsorbed}}$.

The reactions were studied in the range 30–60 °C. Some experimental results, along with the simulated curves, for the first 25 min of reaction are shown in Figures 2–4 for reactions carried out at 37, 48 and 58 °C. Mainly because of differential adsorption phenomena, which will be considered later, the best reproducibility in rates was obtained for the reactions carried out at 48–58 °C. The average results for the reactions at 37, 48, 52·5 and 58 °C are shown in Table 2, where *k* represents the pseudo-first-order rate coefficient for the decay of benzaldehyde in the presence of lithium metal (good correlation factors, >0·98, were usually obtained for each plot).

Table 2. Reaction of benzaldehyde, **1**, with lithium in THF at several temperatures: overall rate constantsand calculated activation parameters[a]

Temperature (°C)	Concentration (M)		Rate constant,
	$[\mathbf{1}]_0$	[Li]	$10^4\,k$ (s^{-1})
37	0.23	3.9	7 ± 1.2
48	0.22	2.4	8 ± 0.7
52.5	0.24	2.4	13.8 ± 0.5
52.5	0.16	3.4	13.2 ± 1.5
58	0.23	2.3	17.2 ± 1.0

[a] $\Delta H^{\ddagger} = 60 \pm 13$ kJ mol^{-1}; $\Delta S^{\ddagger} = -117 \pm 42$ J K^{-1} mol^{-1}.

As examples, the rates of reactions with two different relative amounts of **1** and lithium are shown for reactions carried out at 52·5 °C. At temperatures less than 48 °C, the reaction is more sensitive to reaction conditions such as relative reactant concentrations and overall area of the lithium metal, and the rate of disappearance of **1** departs from pseudo-first order, probably owing to the increased adsorption effects. In fact, Arrhenius plots for reactions carried out below 40 °C exhibit smaller activation enthalpy (not shown) than that given in Table 2.

These results, together with the observed induction period, may indicate that most of the reaction at low temperatures occurs on the adsorbed benzaldehyde layer. Frequently, a heterogeneous reaction has a lower activation energy than the same reaction under homogeneous conditions. Consistent with this interpretation, it was observed that the percentages of adsorbed (recovered) benzaldehyde are greater at low than at higher temperatures.

Evidence for the radical intermediates

Trapping with carbon tetrachloride

Ingold *et al.*,[12] studied the reaction of carbon tetrachloride with the benzoyl radical, **5**, generated by laser flash photolysis (LFP), which produces benzoyl chloride, **6**:

$$\underset{\mathbf{5}}{\mathrm{PhCO}^{\bullet}} + \mathrm{CCl_4} \rightarrow \underset{\mathbf{6}}{\mathrm{PhCOCl}} + {}^{\bullet}\mathrm{CCl_3} \qquad (2)$$

In the present case, taking into account that the expected amounts of free radical would be low, the reactions were carried out under different conditions and a careful search for products was carried out in all cases. Some results are shown in Table 3. [The detection limit (LD) and quantification limit (QL) for benzoyl chloride were determined to be 2×10^{-4} and 5×10^{-4} M, respectively.] Aliquots were taken

Table 3. Reaction of benzaldehyde, **1**, with lithium metal in THF and addition of carbon tetrachloride: quenching with acetic anhydride

Reaction conditions	Temperature (°C)	Reaction time (min)	Concentration in solution(10^{-2} M)			
			[**1**]	[**8**]	[**6**]	[**7**]
A[a]	37.5	3	10.0	0.4	0.3	—
		equil.[d]	2.0	—	—	3.5
B[b]	37.5	20	8.6	0.06	3.9	0.2
		equil.[d]	1.5	0.85	5.0	4.0
C[c]	25	45	8.2	0.75	4.9	1.7
		equil.[d]	1.0	3.7	6.0	4.0

[a] $[\mathbf{1}]_0 = 0.25$ M, $[\mathrm{Li}]_0 = 3$ M; aliquots of the reaction mixture were taken at the times shown, added to CCl_4 and allowed to react for 24 h.

[b] $[\mathbf{1}]_0 = 0.20$ M, $[\mathrm{Li}]_0 = 4$ M. CCl_4 was added to the reaction flask after 5 min to give $[CCl_4] = 0.24$ M.

[c] $[\mathbf{1}]_0 = 0.21$ M, $[\mathrm{Li}]_0 = 3$ M, $[CCl_4] = 0.22$ M (added immediately after **1**).

[d] Time at which equilibrium was reached.

at relatively early times of reaction up to the time of no further observed decrease in [**1**], which is called 'the equilibrium time' (eq) in Table 3. Since in this reaction the main product is benzyl alcohol, some esterification occurs in the reaction mixture by reaction with *in situ* formed **6**, giving benzyl benzoate, **7** [equation (3)]. The reaction mixture was further quenched with acetic anhydride, which transforms **2** into the benzylacetate, **8** [equation (4)].

$$\mathrm{PhCOCl + PhCH_2O^- \rightarrow \underset{\mathbf{7}}{PhCO_2CH_2Ph} + Cl^-} \qquad (3)$$

$$\mathrm{PhCH_2O^- + (CH_3CO)_2O \rightarrow \underset{\mathbf{8}}{CH_3CO_2CH_2Ph}} \qquad (4)$$

In all cases, **6**, **7** and **8** were detected in variable amounts. It can be observed in Table 3 that in the presence of carbon tetrachloride the amounts of trapped products increased, as expected from the high reactivity of **5**. (When the reaction was quenched with an aqueous solution of ammonium chloride, benzoic acid was detected instead of **6**.)

Reaction with carbon monoxide

The effect of adding CO was examined under different conditions, since CO is a known one-electron oxidant toward this type of radical.[11] In all cases, the reactions were allowed to proceed for 48 h. As a reference, the reaction was carried out in the absence of CO (reaction conditions A in Table 4). CO was flushed immediately after adding **1** (reaction conditions B) or 15 min after the addition of **1** (reaction conditions C). It can be observed in Table 4 that when the reaction was carried out in the presence of CO the amount of **1** recovered increased with respect to the reference reaction, the production of bibenzyl, **9**, diminished, and some new products from the reaction with the solvent appeared. The increase in **1** recovered (greater when the CO was added after 15 min) and the decrease in the production of **9** are consistent with a decrease in the concentration of **5** due to its oxidation by CO.

The role of CO in the production of the higher molecular weight products (MW > 300) is not yet completely clear. Nevertheless, we have observed the formation of complexes between organolithium radicals and radical anions with CO, in addition to the production of radicals from the reaction of napthyllithium with THF. It is likely that under the present reaction conditions complexation of the initially formed **5** favors proton abstraction from THF and the coupling reactions of both radicals, forming the high-MW products.

EPR measurements

The EPR spectra of the reaction mixtures obtained under several reaction conditions were measured. No evidence for **5** was detected, which is reasonable taking into account its high instability compared with the EPR recording time-scale. In all cases, good resolved spectra were obtained and the pattern of the benzil radical anion was clearly recognized (Figure 1).

Table 4. Reaction of benzaldehyde, **1**, with lithium in THF at 25 °C in the presence of carbon monoxide: reaction time = 48 h; quenching with saturated solution of NH_4Cl[a]

Reaction conditions	Concentration (%)				
	1	**2**	**3**+**4**	**9**	Unknown
A[b]	2.5	42.5	11	19	16
B[c]	16	41	14	2	20
C[d]	30	28	14	—	20

[a] $[\mathbf{1}]_0 = 0.5$ M, $[\mathrm{Li}]_0 = 2$ M.

[b] Reaction without CO.

[c] CO added immediately after **1**.

[d] CO added 15 min after **1**.

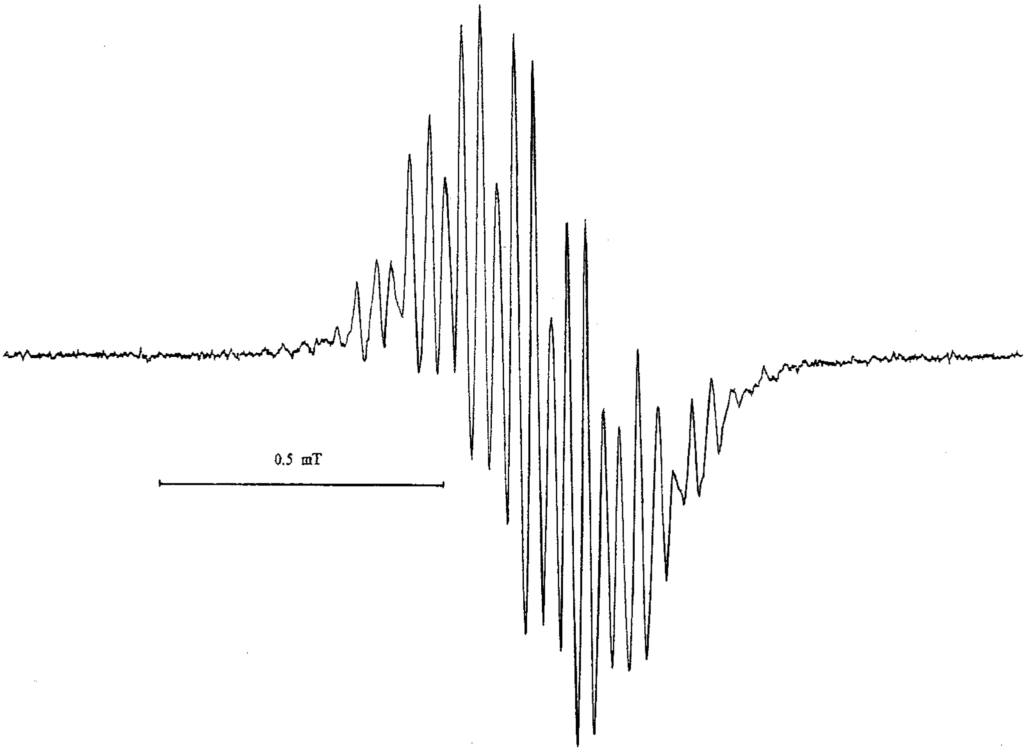

Figure 1. EPR spectrum of the reaction mixture of benzaldehyde with lithium metal in THF. Modulation amplitude 10 = 1.6] gain 10^{-5} = 4; spectral width Δ = 0.9 mT (coincident with the EPR spectrum of benzil radical anion under the same conditions)

EPR spectra were recorded for reactions using [**1**] = 0·66 M and [Li] = 1·6 M. At 30 °C the maximum intensity was reached after 43 min whereas at 67 °C, the maximum intensity was reached immediately. The observed hyperfine splitting constants (0·111, 0·054 mT) are consistent with the calculated HFSC for the benzil radical anion (0·132, 0·038 and 0·138 for *ortho*, *meta* and *para*, respectively). To confirm the structure, a solution of 0·66 M benzil in THF was treated with lithium (to give [Li] = 1·6 M) and the EPR spectrum recorded. A spectrum coincident with that shown in Figure 1 was obtained.

$$\underset{\mathbf{1}}{\mathrm{PhCHO}} + \mathrm{Li} \xrightarrow{k_1} \mathrm{PhCHO/Li}$$

$$\mathrm{PhCHO/Li} \xrightarrow{k_2} \underset{\mathbf{10}}{[(\mathrm{PhCHO})^{\bullet -}, \mathrm{Li}^{+}]}$$

$$\mathrm{PhCHO} + (\mathrm{PhCHO})^{\bullet -} \xrightarrow{k_3} \mathrm{PhCH_2O^{-}} + \mathrm{PhCO^{\bullet}}$$

$$\mathrm{SH} + (\mathrm{PhCHO})^{\bullet -} \xrightarrow{k_4} \mathrm{PhCH_2O^{-}} + \mathrm{S^{\bullet}}$$

$$\mathrm{SH} + (\mathrm{PhCO})^{\bullet} \xrightarrow{k_5} \mathrm{PhCHO} + \mathrm{S^{\bullet}}$$

Scheme 1

$$\underset{\mathbf{1}}{\mathrm{PhCHO}} + \mathrm{Li} \xrightarrow{k_1} \mathrm{PhCHO/Li}$$

$$\mathrm{PhCHO/Li} \xrightarrow{k_2} \underset{\mathbf{10}}{[(\mathrm{PhCHO})^{\bullet -}, \mathrm{Li}^{+}]}$$

$$\mathrm{PhCHO} + (\mathrm{PhCHO})^{\bullet -} \xrightarrow{k_3} \mathrm{PhCH_2O^{-}} + \mathrm{PhCO^{\bullet}}$$

$$2\ \mathrm{PhCHO^{\bullet}} \xrightarrow{k_4} \underset{\mathbf{4}}{\mathrm{PhCOOPh)^{\bullet}Li^{+}]}}$$

$$\underset{\mathbf{4}}{\mathrm{PhCOCOPh}} + \mathrm{Li} \xrightarrow{k_5} \underset{\mathbf{11}}{[(\mathrm{PhCOCOPh})^{\bullet}\mathrm{Li}^{+}]}$$

$$(\mathrm{PhCOCOPh})^{\bullet} + \mathrm{PhCHO} \xrightarrow{k_6} \underset{\mathbf{12}}{\mathrm{PhCOCOHPh^{-}}} + \mathrm{PhCO^{\bullet}}$$

$$\mathrm{PhCO^{\bullet}} + (\mathrm{PhCHO})^{-} \xrightarrow{kx_7} \mathrm{PhCOCOHPh^{-}}$$

$$\mathrm{SH} + (\mathrm{PhCHO})^{\bullet} \xrightarrow{k_8} \mathrm{PhCH_2O^{-}} + \mathrm{S^{\bullet}}$$

Scheme 2

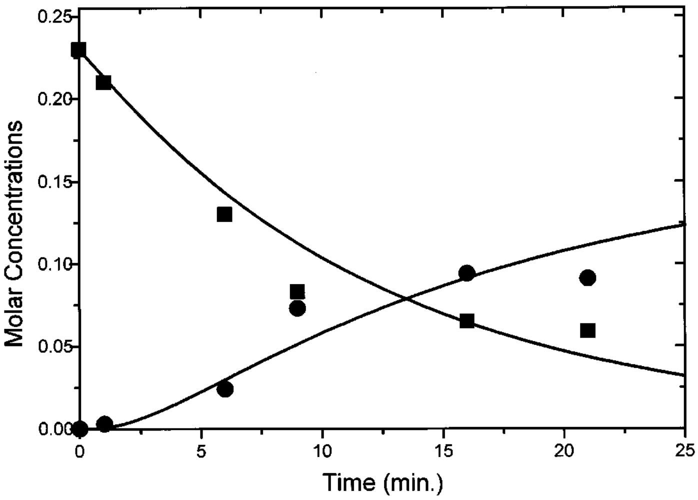

Figure 2. Reaction of benzaldehyde with lithium in THF at 37 °C. Experimental data: ■, benzaldehyde; ●, benzyl alcohol. Simulated curves

Solvent effects

We have previously observed that related reactions of organolithium compounds are highly sensitive to the features of the medium, since it influences the aggregation of the reactants.[13] In order to determine the effect of a solvent less basic and less polar than THF, **1** was allowed to react with Li metal in hexane. It was found that the overall decay of benzaldehyde was slower than in THF, a new reaction product, benzyl benzoate, **7**, was isolated as the major product formed in 81–99% yield. In every case, under various reaction conditions, there was a clean reaction with a high conversion to **7**. The potential of the reaction as a synthetic tool is currently under investigation.

The inverse reaction, i.e. decomposition of the benzyl benzoate radical anion, has recently been studied in ethanol and in hexane.[14] Benzyl benzoate was reduced by solvated electrons generated by pulse radiolysis, $k_e = (5 \pm 1) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$, and the first-order decomposition rate was $4{\cdot}8 \times 10^4\ \text{s}^{-1}$ in ethanol and $2{\cdot}2 \times 10^5\ \text{s}^{-1}$ in hexane.[15] Although the authors did not detect appreciable amounts of benzoyl radical in this reaction, pulse radiolysis of a solution of benzoic anhydride showed that fragmentation occurs to afford the benzoyl radical.[16,17]

In the present case, hydrogen-atom abstraction by **5** from hexane should be slower than that from THF, and the same would be expected for the electron transfers, as observed for other related SET reactions.[18] On the other hand, the benzoyl radical and the benzyl alcohol anion (step 3) are expected to remain longer in the solvent cage, allowing reaction within the cage before diffusion occurs (see Scheme 1). As a result, the benzyl benzoate radical anion is formed, which could transfer an electron to unreacted **1**, producing **7**, and a fresh benzaldehyde radical anion. This reaction scheme explains not only the production of **7**, but also the absence of substantial amounts of **4**. Reaction within the cage in the double layer at the surface metal prevents the accumulation of **5**, which is required for dimerization.

Treatment and discussion of the kinetic results

Kinetic studies on non-electrochemical reactions that occur at liquid–solid interfaces are very scarce, and quantitative treatments have been discouraged by the heterogeneous nature of the reactions. It has been found that lithium dialkylamides behave as single-electron donors toward benzophenone,[19] and we have recently characterized the benzophenone radical anion in the reactions of phenyllithium with CO, by ^{13}C NMR[20] and ESR[21] spectroscopy. On the other hand, previous studies suggest that LDA reacts with benzophenone by a polar mechanism in which a hydride is transferred to the ketone.[22] Kowalski *et al.*[22] proposed that the mechanism of the reaction of benzophenone with LDA to produce benzhydrol proceeds via a six-centered transition state. Newcomb and co-workers[23,24] reported similar results in reactions when a β-hydride ion is transferred from LDA to benzophenone to produce benzhydrol.

To our knowledge, the first analytical steady-state solution for a somewhat similar system is that developed by Garst *et al.*,[25] called a simplified ‘D model,’ which was applied to describe the mechanism of Grignard reagent formation. A similar, albeit more simplified, approach will be followed here; it includes first-order surface reaction steps and first- and second-order solution steps.

A simplified reaction scheme is first proposed to calculate the limiting conditions, which is shown in Scheme 1. The observed adsorption phenomena (symbolized by PhCOH/Li) are considered as the first step and the overall rate of adsorption measured by $k_1 = 8 \times 10^{-4}\ \text{s}^{-1}$ at 48 °C [Garst *et al.*[25] called it ‘flux’ instead of velocity in order to distinguish

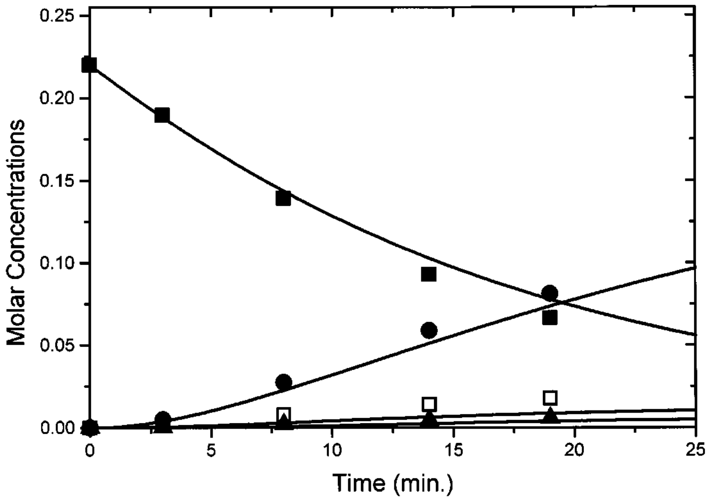

Figure 3. Reaction of benzaldehyde with lithium in THF at 48 °C. Experimental data: ■, benzaldehyde; ●, benzyl alcohol; ▲, benzil; □, benzoin. Simulated curves

an area-based rate (mol cm^{-2} s^{-1}) from the usual volume-based rate; for the sake of simplicity they are not differentiated in the present paper.]

The adsorption step would be followed by one-electron transfer from the lithium surface to the adsorbed benzaldehyde, measured by k_2, forming the radical anion (**10**)–lithium cation pair; **10** escapes the cage, and its further reactions with unreacted **1** or with the solvent SH (k_3 and k_4, respectively) produces the precursor of **2**. The calculated values of k_1 to k_4 (10^2 s^{-1}) are 0·08, 0·08, 17 and 1·7, respectively. The acyl radical **5** reacts with the solvent, regenerating **1**; for THF, k_s is *ca* 6×10^3 s^{-1}. This simplified scheme accounts for the main experimental results, and the calculated *k* values were used as the limiting conditions for a more complex differential equation system based on the overall scheme of reactions shown by Scheme 2.

Apart from the steps already discussed, the other radical reactions that might occur at the metal surface were included to account also for the observed minor products (Scheme 2). Coupling of the benzoyl radical anion (k_4) would produce benzil, **4**, which by electron transfer at the lithium surface could give the radical anion **11** (k_5), which by further reaction with unreacted **1** would produce the benzoin anion, **12** (k_6); **11** could be also produced by the

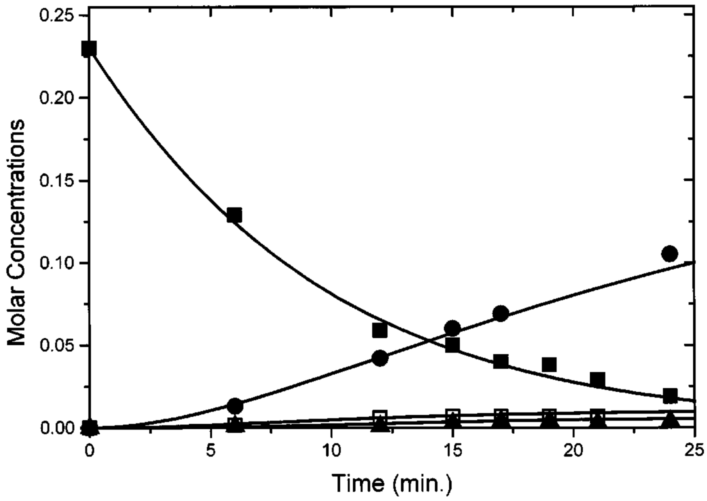

Figure 4. Reaction of benzaldehyde with lithium in THF at 58 °C. Experimental data: ■, benzaldehyde; ●, benzyl alcohol; ▲, benzil; □, benzoin. Simulated curves

Table 5. Reaction of benzaldehyde, AH, with lithium in THF: calculated partial rate constants and some partial activation parameters[a]

Rate constant	Temperature (°C)				$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
	37	48	52	58		
$10^3 k_1 (s^{-1})$	1.25	0.85	1.25	1.67	[b]	[b]
$10^3 k_2 (s^{-1})$	3.33	1.67	3.0	0.8	[b]	[b]
k_3 (M^{-1} s^{-1})	0.58	0.66	1.00	1.08	24 ± 8	-172 ± 25
$10^{-9} k_4$(M^{-1} s^{-1})	8.71	9.64	9.98	10.52	4.97 ± 0.01	-39.4 ± 0.1
$10^4 k_5 (s^{-1})$	3.3	3.3	3.5	12.0	[b]	[b]
$10^3 k_6$(M^{-1} s^{-1})	1.38	2.0	3.0	3.3	35 ± 7	> error
$10^{-3} k_7$ (M^{-1} s^{-1})	1.83	3.3	3.5	4.0	30 ± 5	-86 ± 16
$10^3 k_8$ (s^{-1})	1.67	6.67	9.5	16.7	91 ± 4	-3.3 ± 0.3

[a] Error ⩽ 8 = 10%.

[b] These steps do not follow the Arrhenius equation; they are probably complex steps where adsorption phenomena are present.

reaction of the benzoyl radical with unreacted **1** (k_7). Table 5 gives the calculated rate coefficients; for reactions at 37, 48 and 58 °C and the experimental data and calculated lines are shown in Figures 2, 3 and 4, respectively. The simulated curves account satisfactorily for the disappearance of **1** and also the induction lag, which is more important at the lower temperatures. There is good consistency with the observed data for the formation of products **2**–**4**. At lower temperatures, the formation of products is clearly sigmoid, as expected for the relative major influence of the flux (governed by D, the diffusion coefficient, and δ, the surface reactivity). Higher temperatures help diffusion and favour the electron transfer and second-order reactions in solution. Nevertheless, the net effect of changing D is much more complex since other parameters are D dependent; it is likely that the production and coupling of the radicals are diffusion-controlled, as was observed or assumed for the Grignard reagent formation.[26]

Consistent with the observed results, Table 5 shows that the overall rate of reaction is strongly controlled by the 'adsorption rate,' since most of the subsequent reactions that occur in the solution and/or on the metal surface are faster. Similarly, Ingold *et al.*[12] observed a rate coefficient $k = 5{\cdot}6 \times 10^4$ M^{-1} s^{-1} for the reaction of carbon tetrachloride with the benzoyl radical, **5**, carried out at 24 °C; the kinetics of the reaction in THF were followed by time-resolved infrared spectroscopy (TRIR).[12] The only reaction in Scheme 2 for which the calculated rate was higher than that of equation (2) is the coupling of the radicals measured by k_4. (We have recently measured the kinetics of the reaction of naphthyllithium with CO in THF and the estimated rate of coupling of the naphthoyl radical was *ca* 10^6 M^{-1} s^{-1}).[27] Taking into account that CCl_4 is present in very high concentration compared with that of **5** it is reasonable that relatively small amounts of its reaction product were detected when the reaction was carried out in the presence of 0·24 M CCl_4.

Since reaction with solvent (k_S) is first order whereas coupling (k_c) is second order, the competition is concentration dependent, i.e.

$$\text{rate}_c/\text{rate}_S = 2\,k_C\,[R^{\bullet}]^2/k_S[R^{\bullet}] = 2\,k_C/k_S\,[R^{\bullet}]$$

Typical values for $2k_C$ and k_S in THF are 3×10^9 M^{-1} s^{-1} and 6×10^3 s^{-1}, respectively, for primary alkyl radicals.[25] If the steady-state concentration of $R^{\bullet}$ in THF is 2×10^{-6} M, then the yields of coupling and solvent cleavage are the same. On the other hand, when the radicals are formed at a solid surface, they tend to 'pile up' near it, even if they are freely diffusing in solution.[28] This can result, during the electron transfer, in a steady-state concentration near the surface that approaches or exceeds 10^{-4} M,[25] at which concentration the rate of coupling is about 50 times that of reaction with the solvent. In the present study, the observed values for k_c and k_S at 25 °C are $7{\cdot}25 \times 10^9$ M^{-1} s^{-1} and $5{\cdot}6 \times 10^4$ s^{-1}, respectively. The resulting value of $[R^{\bullet}]$ is $4{\cdot}6 \times 10^{-6}$ M, consistent with the small amounts of coupling products found and a negligible accumulation of **5** on the lithium surface. These results confirms previous studies on the mechanisms of reaction of phenyllithium with CO in THF solution, where **5** is proposed to be a reactive intermediate and coupling products were also observed in small amounts.[11]

Surface effects

The experimental results are clear about the influence of the adsorption effects: the strong interaction between the adsorbate and the metal causes the formation of a layer on the metal surface. This causes the presence of reactant species at the metal surface (or close to the metal surface) in relative amounts higher than the bulk concentration, at the same time the energetics of the reaction of adsorbed species may be different than those of dissolved species, and finally there is the problem of forming a blocking layer on the metal surface.[29] The degree at which adsorption is attained is clearly seen to depend on the bulk concentration and for this reason [**1**] was kept mostly within the range 0·20–0·25 M.

According to the observed results, adsorption of **1** would seem to be a prerequisite for rapid electron transfer (as in electrocayalsis) and is probably responsible for the 'lag' or induction period observed in the formation of **2**. Consistent with this is the fact that the 'sigmoid' behaviour is more pronounced at lower temperatures, with a reduction in the 'lag' as the temperature increases. Nuzzo and Dubois[29] have studied the reaction of methyl bromide with magnesium single crystals and found that CH_3Br is both physisorbed and dissociatively chemisorbed at -150 °C; the results are not altered by coadsorption with dimethyl ether. The chemisorbed species desorbs at a temperature as low as -130 °C.[30]

Some of the important remaining questions concern the nature of the transition state for the step(s) leading to radicals and the nature of the steps leading from them to the products. Some hypotheses are (1) that **1**→**5** occurs at the lithium surface, (2) that **5** is not adsorbed at the surface but instead diffuses freely in solution, where it can dimerize or react with solvent or with other radicals or radical anions, and (3) that the transformation of **5** into products (through several steps) is initiated at the lithium surface and has a rate that is proportional to the concentration of **5** at the surface. Although controversial, the preferred mechanism at present for Grignard reagent formation favors the interpretation in which intermediate alkyl radical do not remain adsorbed.[31] The present results seem also to indicate that $PhCO^{\bullet}$ does not remain adsorbed.

EXPERIMENTAL

Materials. THF was purified as previously described.[32] Benzene was distilled over sodium wire and then refluxed over lithium benzophenone ketyl and distilled immediately prior to use. Hexane was purified by refluxing with concentrated sulfuric acid for 2 h, then distilled and stored over sodium hydroxide pellets; it was distilled over lithium benzophenone ketyl immediately prior to use. Carbon tetrachloride (Carlo Erba) was passed through an alumina column and distilled. Solvents were stored under argon in special vessels that allow delivery without air contamination. Benzaldehyde (UCB) was distilled at reduced pressure under nitrogen and stored under dry argon. Carbon monoxide was generated from the reaction of sulfuric acid with 98% formic acid and treated as described previously.[33] Benzophenone (Fluka) was 99% pure and was used after recrystallization from ethanol. Benzil and benzoin were identified spectroscopically and by their melting points against samples independently prepared by reported methods, and crystallized from ethanol, m.p. 94–95 °C (lit.[32] 94–95 °C) and 135–137 °C) (lit.[34] 135–137 °C), respectively. The lithium benzyl ketyl was prepared by treatment of the benzil in THF solution with a slight excess over the stoichiometric amount of lithium wire, as previously described for the lithium benzophenone ketyl.[20] The concentrations of the organolithium derivatives and of the independently prepared lithium ketyls were determined both by the double titration technique using ethylene 1,2-dibromide and by reaction with diphenylacetic acid.[13]

All glassware, syringes and needles were dried in a vacuum oven and cooled in a desiccator; they were flushed with dry nitrogen immediately before use.

Reactions of **1** *with lithium*. Lithium wire was weighed under ligroin, washed with hexane (then, for reactions in THF, with THF) and cut into small pieces in the reaction flask containing a small portion of solvent, under a stream of dry argon. The reaction flask was capped with an 'air-tight' stopper, and alternatively evacuated and flushed with nitrogen several times. Reagents and solvents were transferred by syringes using techniques described for the manipulation of air-sensitive compounds.[35] The products of the reaction of **1** were isolated and characterized as reported previously for similar reactions.[33] The reactions of **1** with lithium wire in the presence of CO were carried out by the general procedure reported previously for phenyllithium.[32] The amounts of **1** on the lithium surface were determined by difference between $[\mathbf{1}]_0$ and the [**1**] found in solution when no reaction was observed; in the other cases a mass balance was applied, taking into account the amount of **1** reacted. Samples of the reaction mixture were quenched with acetic anhydride or with a saturated solution of NH_4Cl, and analyzed by GC, using an OV-101 column (50–270 °C temperature gradient).

EPR spectra. A Bruker ER 200D (X band) TE102 cavity was used for recording EPR spectra, using procedures similar to those described for the EPR and NMR determinations of the reaction of PhLi with CO.[20, 21] The independently prepared radical anion solutions or the reaction mixtures in preparative concentrations (0·2–1·5 M) were diluted to nearly 10^{-5} M with THF. Optimization of the final concentration was adjusted in each case. The temperature was kept at 0 °C using a Dewar cavity with a thermostated stream of air; measurements at higher temperatures (30–60 °C) showed a fast decrease in the intensity of the signals. Calibration was carried out at different modulation amplitudes using a solution of galvinoxyl in THF.

Kinetic measurements. The reaction was followed by taking 0·2 ml aliquots of the reaction mixture at time intervals, quenching with 1 ml of acetic anhydride and analyzing by GC after 48 h, using benzophenone as an internal standard. The delay allowed complete esterification. Samples of independently prepared standard references were treated similarly and the GC response factors determined in each case. Runs were made at least in triplicate and the reproducibility was satisfactory. In the case of quenching with a saturated solution of NH_4Cl, 0·1 ml was used.

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