Kinetic Study of the Reaction of Naphthyllithium with Carbon Monoxide in Hexane–Tetrahydrofuran Solution

N. Sbarbati Nudelman* and Fabio Doctorovich
Depto. Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pab. II, P. 3, Ciudad Universitaria, 1428 Buenos Aires, Argentina

The rate of the reaction of naphthyllithium, **1**, with CO in 80:20 hexane–tetrahydrofuran (THF) was studied at 25 °C. The determined second order kinetic law was found to be first order with respect to **1** and to CO. The observed specific rate coefficient is 6.63 ± 0.35 $dm^3\ mol^{-1}\ s^{-1}$. Radical scavengers were observed to inhibit the CO uptake: this result, as well as the kinetic studies, are consistent with an electron transfer as the first and rate-determining step of the reaction. The rate of the reaction between **1** and THF was also determined and found to be 10^5 times slower than the reaction of **1** with CO.

There is an increasing recognition that many addition reactions of organolithium[1,3] and organomagnesium[2,4,5] reagents to carbonyl compounds proceed *via* an electron transfer (ET) mechanism. It has been shown recently that in the reaction of aromatic carbonyl compounds with aryllithiums the rate-determining step is the initial ET.[5]

The reactions of aryl-[6] and alkyl-lithiums[7] with carbon monoxide are extensively studied at present since they provide a route to useful synthon intermediates for the preparation of a wide variety of carbonyl functionalized compounds.[7-9] In spite of the synthetic usefulness of these reactions, no mechanistic study has been carried out since the early work by Whitesides.[10] The reactions were usually written as simple polar additions but recent studies in our laboratory by EPR measurements provide evidence that the reactions occur through the intermediacy of paramagnetic species,[11] and suggest that the mechanisms by which these complex reactions proceed could involve ETs.

The more relevant contributions related to ET have been reviewed recently[12] and some of them[13-16] particularly emphasize 'the lessons to be learned from kinetics in describing the ET event'. The present paper describes kinetic measurements of the reaction of naphthyllithium with CO in tetrahydrofuran (THF)–hexane solvents.

Results and Discussion

Reaction of 1-*Naphthyllithium* (**1**) *with THF*.—† The solution of 1-naphthyllithium in THF shows, after a few minutes, an EPR signal that increases with time. Since in the reactions of **1** with CO, radicals were suspected to be key intermediates, it was of interest to examine the above observation, before the study of the reaction of **1** with CO. Although the instability of organolithium reagents in THF solution is well established,[17] to our knowledge there is no report in the literature on the rate of reaction between **1** (or any other related aryllithium) and THF.

The cleavage of THF by organolithiums is widely believed to proceed by way of an initial metallation of the ether,[18] eqns. (1) and (2). Furthermore, the addition of magnesium 2-ethoxyethoxide has been recommended recently, to increase the stability of organolithiums in THF.[19]

$$RLi + \overline{CH_2[CH_2]_3O} \longrightarrow \overline{CH_2[CH_2]_3O}Li + RH \qquad (1)$$

$$\overline{CH_2[CH_2]_3O}Li \longrightarrow CH_2{=}CHOLi + CH_2{=}CH_2 \qquad (2)$$

In the present case, it was observed that the slow reaction of **1** with THF produced an intermediate, that we call **Y**, which shows an UV spectrum with an absorption maximum at 500 nm. The spectrophotometric method, as previously used for similar purposes,[20] was found to be suitable to follow the reaction by measuring the absorbance, *A*, at that wavelength.

The rate of formation of the intermediate, **Y**, with a maximum absorption at 500 nm, is shown by eqn. (3), where *n* and *m*

$$d[\mathbf{Y}]/dt = k[\mathbf{1}]^n[THF]^m \qquad (3)$$

indicate the order with respect to **1**, and to THF, respectively.

The slope, *x*, is related to the concentration of the reactants in a similar way, eqn. (4).

$$x = dA/dt = k'[\mathbf{1}]^n[THF]^m \qquad (4)$$

Table 1 Reaction of naphthyllithium, **1**, with CO in THF at 25 °C. Influence of the initial [**1**][a]

[**1**]/mol dm^{-3}	$10^2\,x\,(A/min)$
0.006	0.159 ± 0.06
0.025	0.420 ± 0.06
0.074	1.386 ± 0.14
0.086	0.732 ± 0.07
0.271	2.460 ± 0.17

[a] *x*, slope of *A vs. t*.

The reaction orders as well as the rate constants were calculated by using the method of the initial rates; good straight lines (*A vs. t*) were obtained for nearly the first 30 min after dissolving the reagent. Table 1 shows the slopes of the lines, *x*, obtained for several initial concentrations of **1**, at 25 °C. For [THF] = *c* (constant), the order *n* was calculated from the plot of ln [**1**] *vs.* ln *x*. An intercept of 0.0609 ± 0.0067 (mol $dm^{-3})^{-0.29}$ s^{-1} and a slope of *n* = 0.714 ± 0.106 (*R* = 0.948) were obtained.

A similar treatment was applied to obtain the order with respect to THF. With the purpose of running the reaction at different concentrations of THF, keeping [**1**] constant, the crystals of **1** were dissolved in varying amounts of THF and then diluted with hexane. It was previously confirmed that **1** was completely stable in hexane solution. Although in this case the solvent is not constant, the information obtained is useful for the

---

† *Compound numbers:* **1**, NpLi; **2**, NpH; **3**, Np_2; **4**, NpBu; **5**, Np_2CO; **6**, $(NpCO)_2$; **7**, NpCOLi; **8**, tetramethylpiperidine *N*-oxyl; **9**, *p*-benzoquinone; **10**, hydroquinone; **11**, quinhydrone; **12**–**17**, see Scheme 1. Np = 1-napthyl.

Table 2 Reaction of naphthyllithium, **1**, with CO in THF–hexane at 25 °C. Influence of the initial [THF][a]

[**1**]/mol dm^{-3}	[THF]/mol dm^{-3}	$10^2\, x$ (A/min)
0.160	4.195	0.090 ± 0.018
0.166	7.372	0.168 ± 0.045
0.154	9.829	0.330 ± 0.090
0.160	12.287	0.720 ± 0.120

[a] x, slope of A *vs.* t.

present purposes. Table 2 shows the slopes, x, of the plots of A *vs.* t obtained for several initial concentrations of THF and constant [**1**], at 25 °C.

The plots of ln [THF] *vs.* ln x give an intercept of $(230 \pm 4.5) \times 10^{-7}$ (mol dm^{-3})$^{-1.22}$ s^{-1} and a slope of $m = 2.22 \pm 0.28$ ($R = 0.967$). Calculation of k' from the reactions carried out at constant [**1**] or at constant [THF] agree satisfactorily and give an average value of $k' = (160.0 \pm 7.3) \times 10^{-6}$ (mol dm^{-3})$^{-1.94}$ s^{-1}.

The calculated fractional orders are indicative of aggregates which are common in organolithium compounds.[21] They also indicate a complex reaction leading to other products apart from a proton abstraction from the solvent, as previously proposed [eqns. (1) and (2)].[18]

A solution of **1**, immediately after it was dissolved in THF, showed a very weak EPR signal. After nearly 30 min the signals had increased, but even after 90 min, no signal was detected under the EPR conditions used to study the reaction of **1** with CO;[11] thus it was clear that the radicals formed between **1** and THF would not interfere in the study of the above reaction which is complete in a few minutes.

The solution of **1** and THF gave a reasonably well resolved EPR spectrum after 3 h 'reaction'. The spectrum showed a quintet with lines of multiplicity, which could be consistent with the naphthalene radical forming an 'inner sphere' ternary complex where one electron has been transferred to the THF molecule through the cation. A similar complex was previously proposed for the spin density transfer from the lithium benzophenone ketyl to the THF nuclei.[22] Simulation of the EPR spectrum with a computer program developed by Joela[23] allowed calculation of the hyperfine splitting constants to be 4.40, 0.60 and 0.36 G, respectively. There are no recent reports of the EPR spectrum of the naphthalene or the naphthyl anion radicals. The hyperfine constants reported previously were 4.792, 1.788 and 1.213 G,[24] for the lithium naphthalene radical in dioxane. Although these values differ from those obtained under the present conditions, taking into account the kinetic as well as the GC results, it is reasonable to assume that the EPR spectrum corresponds to a complex mixture where the naphthalene radical is a main component.

The GC analysis of different reaction mixtures (t = 48 h) showed two main products: naphthalene (**2**) (45%) and bi-1,1'-naphthyl (**3**) (37%); several other unidentified products of higher retention times were also formed in small amounts. When the solution of **1** was treated with an excess of butyl bromide, shortly after solid **1** was dissolved in THF, only a small amount of naphthalene (5–8%) and 1,1'-binaphthyl (3–5%) were obtained, apart from the product of **1** with BuBr: 1-butylnaphthalene, **4** (> 90%).

Taking into account these results, in all the following studies, solid **1** was dissolved immediately prior to use, avoiding long contacts with the solvent.

Reaction of 1*-Naphthyllithium* (**1**) *with* CO.—The products of the reaction of **1** with CO were previously[25] identified as: di-1-naphthyl ketone (**5**) and bi-1,1'-naphthoyl (**6**), eqn. (5) (Np = 1-naphthyl).

Table 3 Solubility of CO in organic solvents at 25 °C, p = 1 atm

Solvent	$10^3\,\alpha$[a]	$10^3\,\alpha$
Toluene	166	166[b]
Acetone	220	218[b]
Hexane	170	
THF	267	
Hexane–THF (80:20)	178	

[a] α: CO volume (at 0 °C) dissolved in a solvent volume unit at 25 °C. [b] Ref. 28.

$$\mathrm{NpLi}\ (\mathbf{1}) + \mathrm{CO} \longrightarrow \mathrm{Np_2CO}\ (\mathbf{5}) + (\mathrm{NpCO})_2\ (\mathbf{6}) \quad (5)$$

We have recently developed a ^{13}C NMR method,[26] to determine radical anions in concentrations similar to those found under preparative conditions. Studies of the reactions of **1** with CO indicate that radicals are involved as true reaction intermediates.[27] On the other hand, the ^{13}C NMR behaviour of the radical anion of **6**, independently prepared, shows a close correspondence with that of the reaction mixture of **1** with CO in THF solution.[27] The same applies to both EPR spectra.

Several difficulties should be overcome so as to measure the rate of the reaction of **1** with CO; *e.g.*, (*a*) the high rate of the carbonylation reaction in THF, together with the inapplicability of the stopped-flow technique—to slow the rate down a co-solvent of low polarity, hexane, was added; even so the reaction was complete in a few seconds; (*b*) the high extinction coefficient of the intermediates—this fact hinders measuring of the absorbance at the maximum wavelength (*ca.* 350 nm)—on the other hand, no reaction occurs at concentrations of the reagent below 0.018 mol dm^{-3}; (*c*) the high sensitivity of the reagent to humidity and oxygen, that prevents conventional manipulations such as ample range of dilution, *etc.*—quartz UV cells furnished with a graded tube capped with a rubber septum were used throughout all the experiments; the cell was evacuated and flushed with nitrogen, alternately several times, to ensure complete inert atmosphere; (*d*) the fact that this is a heterogenous reaction, which hinders the efficient mixing of reactants—different methods were tried to overcome this difficulty, without losing information about the precise concentrations of both reactants (a difficulty that was observed when using the stopped-flow technique)—the best results were obtained by syringing the THF solution of **1** into the UV cell filled with CO; in this way, the solution is saturated with CO and **1** reacts with the dissolved gas: the reaction stopped when all the dissolved CO was consumed.

Since the solubility of CO under the present reaction conditions was not known,[28] it had to be determined and the data are shown in Table 3. The solubility in toluene and in acetone was also determined to compare with the data previously reported and a good accordance was observed (Table 3). The rate of reaction of **1** with CO was measured in 80:20 (v/v) hexane–THF; in this solvent the molarity of CO at 25 °C is 8.62×10^{-3} mol dm^{-3}.

The rate of reaction of **1** with CO was measured directly in the thermostatted cell at 25 °C by recording the absorbance at 500 nm each 0.3–0.4 s, using a diode-array spectrophotometer. Typical results are shown in Table 4 for three different concentrations of **1** and saturated solutions of CO in 80:20 hexane–THF. It can be observed that when [**1**] = 0.0180 mol dm^{-3} the reaction could be followed for 30 s, for [**1**] = 0.0225 mol dm^{-3} the reaction was over in 20 s and in almost 15 s for [**1**] = 0.03 mol dm^{-3}.

The rates were estimated by examining the fitting of the data (A *vs.* t) to several equations. It was found that very good

Table 4 Reaction of 1-naphthyllithium, **1**, with CO in 80:20 hexane–THF at 25 °C[a]

	[**1**]/mol dm^{-3}		
t/s	0.0180	0.0225	0.0300
3.0	1.171		
4.0	1.398	1.835	
4.5		1.932	1.761
5.0	1.561	2.053	1.938
5.5		2.121	2.065
6.0	1.714	2.200	2.168
6.5			2.252
7.0	1.820	2.326	2.315
7.5			2.388
8.0	1.928	2.424	
8.5			2.457
9.0	2.022	2.443	
10.0	2.111	2.515	
11.0			2.612
12.0	2.227	2.646	
14.0	2.339	2.694	
16.0	2.422	2.748	
18.0	2.512		
20.0	2.535	2.789	
30.0	2.784		
k/dm^3 mol^{-1} s^{-1}	4.18	5.59	5.65

[a] *A vs. t.*

Table 5 Reaction of 1-naphthyllithium, **1**, with CO[a] in 80:20 hexane–THF, at 25 °C. Changes in k_1 with C

	[**1**]/mol dm^{-3}				
C	0.0180	0.0225	0.300	k_1/dm^2 mol^{-1} s^{-1}	Error (%)
0	4.18	5.59	5.65	5.14 ± 0.64	12.4
0.429	6.11	6.89	6.79	6.63 ± 0.35	4.8
0.818	6.38	7.94	7.91	7.41 ± 0.69	9.5

[a] $[\text{CO}]_\text{i}$ 0.00862 mol dm^{-3}; A_∞ = 2.78.

straight lines ($R > 0.99$) were obtained for overall orders of 2 and of 3, but only in the case of overall order 2, with unity stoichiometric coefficients, the calculated specific rate coefficients for different [**1**] were coincident.

The best fitting was obtained with the second order kinetic law shown by eqn. (6), where a stands for the initial [**1**]; and

$$kt = \ln\,[(a - 2x)/(b - 2x)]/2(a - b) \qquad (6)$$

$b = [\text{CO}]_\text{i}$ (i = initial) = 8.62 × 10^{-3} mol dm^{-3}.

The experimental 'infinity absorbance' (A_∞) was 2.78; by assuming that the final concentration of the product (bi-1,1′-naphthoyl,[6]) is half the [CO], the specific absorbance of the intermediate could be calculated. Application of eqn. (6) to the data in Table 4 gives the values of k for each [**1**]. The plot of the right term of eqn. (6) *vs.* t, gives the following correlation coefficients (R) 0.999, 0.996 and 0.997 for the reactions at [**1**] = 0.0180, 0.0225 and 0.030 mol dm^{-3}, respectively. It can be observed in Table 4 that the rate obtained at [**1**] = 0.018 mol dm^{-3}, is smaller than those obtained at higher [**1**]. This is due to the fact that traces of humidity are unavoidable at this high dilution of the reagent, and the actual concentration of [**1**] might be smaller than stated.

The average calculated rate coefficient, k = 5.14 ± 0.64 dm^3 mol^{-1} s^{-1}, is 10^5 times greater than the rate of reaction of **1** with THF; thus, it is reasonable to conclude that this last reaction does not interfere in the time scale of the reaction of **1** with CO.

The reaction of **1** with CO produces two main products: di-1-naphthyl ketone (**5**) and bi-1,1′-naphthoyl (**6**) through an intermediate that, in principle, can be assumed to have the structure of a naphthoyllithium, **7**. It is then reasonable to propose the simplified reaction scheme shown by eqn. (7). Since

$$\text{NpLi}\,(\mathbf{1}) + \text{CO} \xrightarrow{k_1} [\text{NpCOLi}]\,(\mathbf{7}) \begin{cases} \xrightarrow[k_2]{+\mathbf{7}} (\text{NpCO})_2\,(\mathbf{6}) \\ \xrightarrow[k_3]{+\mathbf{1}} \text{Np}_2\text{CO}\,(\mathbf{5}) \end{cases} \qquad (7)$$

the reaction was found to be first order with respect to each reactant, the kinetic law for the formation of the intermediate **7** should have the form of eqn. (8).

$$\text{d}[\mathbf{7}]/\text{d}t = k_1[\mathbf{1}][\text{CO}] - k_2[\mathbf{7}]^2 - k_3[\mathbf{1}][\mathbf{7}] \qquad (8)$$

Since **7** does not accumulate, the steady-state treatment may be applied and eqn. (9) results.

$$k_1[\mathbf{1}][\text{CO}] = k_2[\mathbf{7}]^2 + k_3[\mathbf{1}][\mathbf{7}] \qquad (9)$$

The rates of formation of products **5** and **6** are functions of the reactants' concentrations and of k_2 and k_3, respectively, but assuming that the first step is rate determining, and that **5** and **6** are the only reaction products, the simplification shown by eqn. (10) applies.

$$\text{d}[\mathbf{5}]/\text{d}t + \text{d}[\mathbf{6}]/\text{d}t = k_1[\mathbf{1}][\text{CO}] \qquad (10)$$

Since **1** is in excess, [**1**] could be considered relatively constant in a short range of absorbances (*e.g.*, in the range A = 1.5–2.4 the maximum change would be nearly 25% for the more diluted solution, [**1**] = 0.018 mol dm^{-3}). Writing [**5**] as a function of [**6**] and applying conventional manipulation of the equations, the rate of formation of **6** is given by eqn. (11), where

$$\frac{\text{d}[\mathbf{6}]}{\text{d}t} = k_1\left\{\frac{[\mathbf{1}]_\text{i}[\text{CO}]_\text{i}}{(C+1)} - [\mathbf{6}]\left[[\mathbf{1}]_\text{i}\frac{(C+2)}{(C+1)} + 2[\text{CO}]_\text{i}\right] + 2(C+2)[\mathbf{6}]^2\right\} \qquad (11)$$

C stands for the proportionality constant between the rates of formation of **5** and **6**.

The ratio [**5**]/[**6**] is experimentally observed to be equal to 3/7, then, the influence of the error in the estimates of C can be calculated: *e.g.*, for a variation of 25% in C, (C + 1) and (C + 2) vary only 7% and 4%, respectively.

Taking into account that intermediates leading to products **5** and **6** are the main contributors to the absorbance of the reaction mixture at 500 nm, that all the CO is consumed at the end of the reaction, and that [**5**]/[**6**] is held constant throughout the reaction, [**6**] can be expressed in terms of known factors as shown by eqn. (12).

$$[\mathbf{6}] = A[\text{CO}]_\text{i}/A(C + 2) \qquad (12)$$

The specific rate coefficient k_1, can then be calculated as the slope of the right term of eqn. (13) against time. Table 5 shows three values for k_1 calculated using three extreme estimates for C, namely 0, 0.429 and 0.818 and the average k_1 values, for runs at [**1**] = 0.018, 0.0225 and 0.0300 mol dm^{-3}. It is reckoned that C = 0 corresponds to a complete conversion of **1** to **6**, while the last value corresponds to a rate of formation of **6** slightly higher

Table 6 Reaction of 1-naphthyllithium, **1**, in THF at 25 °C, in the presence of radical scavengers

Inhibitor	Amount[b]/mg	[Trap]/[**1**][c] (%)	V_{CO}[d]/cm^3	Inhibition[e] (%)	ArD[f] (%)
None	—	—	7.4	0	
TEMPO (**8**)	63.0	65.0	0.8	89	0
9	10.0	15.0	0.8	88	85
10	10.0	15.0	2.0	73	87
11	8.5	6.4	1.1	85	82
9 + **10** (1:1)	3.0	4.5	1.6	78	88

[a] In all cases 1.5 cm^3 of a 0.4 mol dm^{-3} solution of **1** in THF was used. [b] Weight of radical trap in 1.5 cm^3 of a 0.4 mol dm^{-3} solution of **1** in THF. [c] Moles of trap per 100 mol of **1**. [d] Volume of CO consumed during 10 min carbonylation. [e] Calculated according to V_{CO}. [f] [1-^{2}H]Naphthalene obtained after hydrolysis with D_2O.

than that of **5**. It can be observed in Table 5 that all the values calculated for [**1**] = 0.018 mol dm^{-3} are smaller than the others, due to the previously noted effect of dilution upon [**1**]. On the other hand, it can be observed that k_1 increases with C, this is mainly due to the weight of the term $(C + 1)$ in eqn. (13), that

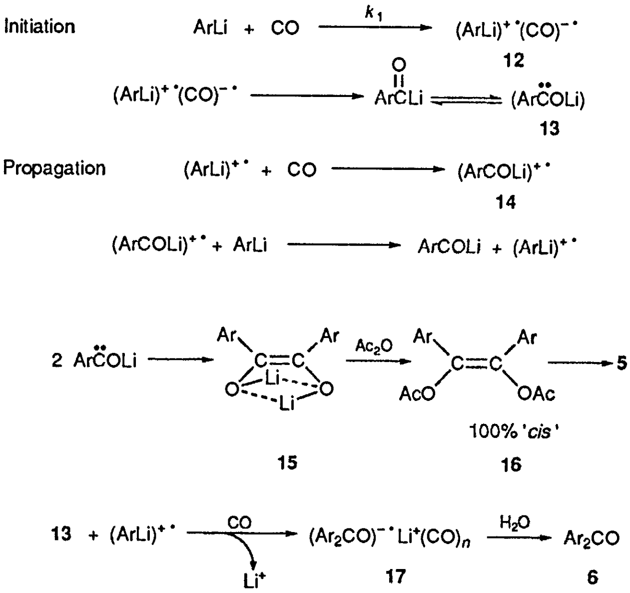
$$k_1 t = \left[\frac{(C+1)}{[\mathbf{1}]_i(C+2) - [\mathrm{CO}]_i 2(C+1)}\right] \times \ln\left[\frac{(C+2)\{2(C+1)[\mathbf{6}] - [\mathbf{1}]_i\}}{2(C+1)\{(C+2)[\mathbf{6}] - [\mathrm{CO}]_i\}}\right] \quad (13)$$

measures the contribution of the rate of formation of product **5**. It is worth noticing that the smaller dispersion in the calculated k_1s are observed for $C = 0.429$, which corresponds to the ratio $[\mathbf{5}]/[\mathbf{6}] = 3/7$ that was observed experimentally, under preparative as well as kinetic conditions. The average calculated value for k_1 is 6.63 ± 0.35 dm^3 mol^{-1} s^{-1}.

The influence on k_1 of variations in $[\mathrm{CO}]_i$ was also calculated. Nearly the same final absorbance was observed [$A_\infty = 2.78$ ($\pm 5\%$)] at the three concentrations of **1** studied. Since A_∞ is directly related to the initial [CO] it can be concluded that this is the same in all the reactions. Nevertheless, a slight change in $[\mathrm{CO}]_i$ does not change the good correlation ($R > 0.99\%$), *e.g.*, for $C = 0.429$ and $[\mathrm{CO}]_i = 0.0130$ mol dm^{-3}, $k_1 = 9.15 \pm 0.65$ dm^3 mol^{-1} s^{-1}; while for $[\mathrm{CO}]_i$ 0.0060 mol dm^{-3}, $k_1 = 5.63 \pm 0.78$ dm^3 mol^{-1} s^{-1}. Thus, even if there were small errors in the estimation of [CO] and of C, the calculated values of k_1 are within acceptable ranges.

Reactions in the Presence of Radical Traps.—To elucidate the role of radicals in the reaction of **1** with CO, the influence of different radical traps was examined and the results are gathered in Table 6, where the ratio [trap] : [**1**] is indicated as the moles of trap per 100 moles of [**1**]. The inhibition (%) was calculated as the decrease in the CO uptake taking as a reference the volume of CO (7.4 cm^3) consumed under normal conditions in the absence of radical inhibitors. The reaction mixture was then quenched with D_2O and the yield (%) of deuteriated naphthalene indicates the amount of unreacted 1-naphthyllithium (**1**) and/or of naphthyl radical recovered. The inhibition (%) was also checked against the GC analysis of the reaction mixtures.

The first radical inhibitor used was tetramethylpiperidine *N*-oxyl (TEMPO) (**8**), which is very well known as a good radical inhibitor. It was observed that relatively small amounts (*e.g.* 10%) have no noticeable effect on the volume of the CO uptake, and that relatively high amounts are needed to considerably decrease the CO absorption and the concomitant disappearance of the brown colour of the reaction mixture. Further treatment of the reaction mixture with D_2O results in recovery of almost 90% of undeuteriated naphthalene. This is indicative that the radical trap TEMPO has reacted with **1** and that is not so appropriate for the study of the reaction with CO.



Scheme 1

Quinones and hydroquinones can produce stable radicals by one electron uptake or donation; since in the present reaction electron transfer is suspected to be the first step, they were considered adequate to test this hypothesis. The reaction of naphthyllithium with CO in THF at 25 °C was examined in the presence of *p*-benzoquinone (**9**), hydroquinone (**10**) and quinhydrone (**11**) as radical inhibitors. It can be observed that quinhydrone (**11**) is a more efficient inhibitor than **9** or **10**, while the mixture of **9** + **10** (1 : 1) is more effective than any of the separate inhibitors. Although both **9** and **10** can react with organolithium compounds, the addition reactions are slow under the present reaction conditions (it has been found, for instance, that 1,2-addition of phenyllithium to **9** requires 8 h)[29,30] and in all cases they occur in an amount not greater than 15%. In fact, when a mixture of **1** with **9** in THF was kept at room temperature and then hydrolysed with D_2O, 86% of [1-^{2}H]napththalene was obtained; the same reaction with **10** or with **11** gave 87% and 84% of [1-^{2}H]naphthalene, respectively. On the other hand, dibenzylacetone, another radical inhibitor, does not produce any important effect.

Mechanism of Reaction.—The kinetic law found for the reaction of **1** with CO is consistent with a first step, involving the reaction of one molecule of aryllithium with one molecule of CO. This result, together with the CO uptake inhibition produced by the radical inhibitors, suggests electron transfer from the aryllithium compounds to the CO, forming the radical cation–radical anion pair, **12**, Scheme 1. (Most of the lithium intermediates shown in the Scheme are probably in the form of aggregates with THF as revealed by the ^{13}C NMR measurements,[26] but they are written as monomers for the sake of clarity.)

Organolithium compounds have been shown to be good one-electron donors[2] to carbonyl compounds, and CO is a known electron deficient compound, and an effective one-electron oxidant toward a variety of aromatic radical ions and dianions.[10,31,32] On the other hand, it has been shown that the enthalpy of formation of the pair $(Ar_2CO)^{\bullet -}(Na)^+$ is 30 kcal mol^{-1} * smaller than the enthalpy of formation of the radical anion $(Ar_2CO)^{\bullet -}$.[33] Many recent works report ET from Grignard reagents[1a,4,34] or from organolithium compounds[5,35] as the first step in the addition to carbonyl compounds, and Yamataka *et al.* reported that the magnitude of the carbonyl carbon kinetic isotope effect (KIE) as well as the absence of substituent effects in the reactions of butyllithium with carbonyl compounds, suggest that the initial ET step is rate determining.[5]

In the present case, the ET measured by k_1, Scheme 1, would be the slower step in the overall reaction. [A huge decrease in rate was observed upon addition of lithium complexing donor bases such as DABCO (1,4-diazabicyclo-[2.2.2]octane) or TMEDA (*N,N,N',N'*-tetramethylethylenediamine), which suggests that lithium is involved in the activation of CO.] The radical pair, **12**, can then react within the cage affording the acyllithium intermediate, which is postulated to be in equilibrium with a carbenoid structure, **13**. Carbene-like intermediates have been reported in the reactions of actinide[35] and other metal[7a,c,8,36,37] complexes with CO and coupling of those oxy-carbene intermediates produces enediolates. We have previously shown[25] that the precursor of **6** is the *cis*-dilithium enolate of naphthoin, **15**, since work-up of the reaction mixture with acetic anhydride produces the (100%) *cis*-diacetate of naphthoin enolate, **16**. The coupling of two carbene-like acyllithiums, **13**, would stereospecifically form the *cis*-lithium dienolate, **15**. Isolation of the naphthoin was possible only when working under an inert atmosphere: in the presence of air, the corresponding diacetate enolates are spontaneously hydrolysed and oxidized to **6**.

The radical cation in **12** can partially escape the cage; the capture of $(ArLi)^{\bullet +}$ by **13** under CO atmosphere, produces the ketyl **17**, which was detected by EPR of the reaction mixtures. It is proposed that the ketyl is coordinated to CO molecules which produce a one-electron oxidation to **5** during the work-up.

The radical cation could also dissociate to an $Ar^{\bullet}$. The $Ar^{\bullet}$ could either dimerize (giving Np_2, **3**) or capture a proton from the solvent giving NpH, **2**. Both by-products, **2** and **3**, have been detected as minor components in the carbonylation reactions, **3** being the main by-product. Walling[38] reported a value of 2×10^9 s^{-1} for the rate of dimerization of alkyl radicals, while the rate of proton abstraction from the THF by a phenyl radical was found to be 4.9×10^6 s^{-1}. In view of the small amounts of by-products **2** and **3** detected, it is reasonable to assume that the reaction within the cage to form **13**, and/or the propagation steps, are faster. Since the diffusion rate is $k_d = 5 \times 10^9$ s^{-1},[39] and the proportion of reaction that occurs within the cage, is nearly $k_c/(k_c + k_d)$ (where k_c stands for the reaction within the cage), the magnitude of k_c should be not less than 10^9 s^{-1}. The $Ar^{\bullet}$ could also react with CO giving the acyl radical, $NpCO^{\bullet}$; nevertheless, the kinetics of the capture of $CH_3^{\bullet}$ by CO has been recently measured and found to be 2.0×10^6 dm^3 mol^{-1} s^{-1} in aqueous solution at 25 °C.[40] Thus, the rate of capture of $Ar^{\bullet}$ by CO in THF, is unlikely to compete with the others under the present reaction conditions.

Conclusions

The present work affords evidence that is consistent with the occurrence of electron transfer from the naphthyllithium to carbon monoxide as the first step of the carbonylation reaction of naphthyllithium. Kinetics indicate that the reaction is first order in naphthyllithium and first order in CO, while the effect of some radical inhibitors suggests that a chain mechanism is involved. The precursors for the two main products, di-1,1-naphthoyl and di-1-naphthyl ketone were fully characterized and the NMR and EPR spectra of the reaction mixtures were consistent with the proposed intermediates.

Experimental

Materials.—Tetrahydrofuran (THF) was purified as previously described.[9a] 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 sulfuric acid (conc.) for 2 h, then distilled and stored over sodium hydroxide pellets; it was distilled over lithium benzophenone ketyl immediately prior to use. Carbon monoxide was generated from the reaction of sulfuric acid with 98% formic acid and treated as previously described.[8b] Benzophenone (Fluka) was 99% pure and was used after recrystallization from ethanol. 1-Naphthyllithium was prepared followed a procedure similar to that previously described,[25] using 1-bromonaphthalene (0.56 cm^3, 4 mmol) and butyllithium in hexane (4.7 cm^3, 4 mmol; 0.85 mol dm^{-3}), at 40–50 °C for 45 min; δ_C(THF; C_6D_6) 188.3, 140.4, 138.5, 133.7, 128.4, 128.3, 126.2, 124.0, 122.8 and 121.7.

Di-1-naphthyl ketone (**5**) and bi-1,1'-naphthoyl (**6**) were identified spectroscopically and by their m.p. against samples independently prepared by reported methods, m.p. 192–194 °C (lit.,[41] 190–191 °C) and 101–102 °C (lit.,[42] 103–104 °C), respectively. The lithium binaphthoyl ketyl was prepared by treatment of the bi-1,1'-naphthoyl in THF solution with a slight excess of lithium wire, as previously described for the lithium benzophenone ketyl;[26] δ_C(THF) 186.5, 143.0, 124.0 and 122.2. The concentrations of **1** and of the independently prepared radicals were determined both by the double titration technique using ethylene 1,2-dibromide, and by reaction with diphenylacetic acid.

All glassware, syringes and needles were dried in a vacuum oven and cooled in a desiccator.

Reactions with Carbon Monoxide.—The reactions of **1** with CO were carried out by the general procedure reported previously for phenyllithium,[9a] using techniques described for the manipulation of these air-sensitive compounds.[43] The products of the reaction of **1** were isolated and characterized as previously reported.[25] The colourless solution turns to bright green at the beginning of the reaction changing to red after 10 min; the CO absorption was complete in less than 30 min. The reaction mixture was treated with saturated NH_4Cl. The solvent of the dried ($MgSO_4$) organic layer was removed under reduced pressure, and the yellow residue was crystallized (methanol).

Reactions in the Presence of Radical Inhibitors.—The reactions were carried out similarly to the general procedure already described, in a reaction flask containing a weighed amount of inhibitor. The inhibition (%) was calculated as the decrease in the CO uptake taking into account the volume of CO (7.4 cm^3) consumed in the absence of radical inhibitors. The effects of these radical inhibitors were also clearly evident through a change in the colour observed at the beginning of the reaction, to an orange coloured mixture at the end of the reaction. The yield (%) of deuteriated naphthalene indicates the amount of unreacted 1-naphthyllithium and/or of naphthyl radical recovered after hydrolysis with D_2O. The inhibition (%)

---

* 1 cal = 4.184 J.

was also checked against the GC analysis of the reaction mixtures: a good agreement was found between the global product yields and the inhibition (%), the ratio [**5**] : [**6**] obtained in the presence of **9**, **10** or **11** did not change with respect to the reaction carried out in the absence of these compounds.

NMR Measurements.—A Varian XL-100 NMR spectrometer was used for recording the ^{13}C NMR spectra. C_6D_6 in a concentric cell was used as external lock for measurements in pure THF. A septum-capped ordinary NMR tube was evacuated and then flushed with pure nitrogen; several vacuum–nitrogen cycles ensured the complete removal of air and its replacement by nitrogen. The radical anion solutions or the reaction mixtures after appropriate treatment were then syringed into the NMR tube.

EPR Spectra.—A Bruker ER 200t (X band) TE102 cavity was used for recording the EPR spectra. They were determined at room temperature using the same tubes and procedure described for the NMR measurements. The independently prepared radical anion solutions or the reaction mixtures in preparative concentrations (0.2–1.5 mol dm^{-3}) were diluted up to nearly 10^{-5} mol dm^{-3} with THF. Optimization of the final concentration was adjusted in each case.

Kinetic Measurements.—The initial rates of reaction between **1** and THF were followed by measuring the absorbance at 500 nm of different initial [**1**] at constant [THF], and *vice versa*. The rate of the reaction of **1** with CO was measured spectrophotometrically, using a diode array Hewlett Packard model 8051 spectrophotometer, recording the absorbance each 0.4–0.6 s. The wavelength of maximum absorbance of the product is 350 nm, but the absorbances were recorded at 500 nm. The reactions were followed directly in the septum-capped thermostatted cells of the spectrophotometer, previously treated as described for the NMR tubes, to assure an inert atmosphere. The initial concentration of CO was equal to its solubility in the solvent used and was determined to be 8.62×10^{-3} mol dm^{-3}. The initial concentration of **1** in these experiments was in the range $(1.8–3.0) \times 10^{-2}$ mol dm^{-3}. The initial rates were given by the slopes of the lines obtained by plotting *A vs. t*. Different kinetic orders were considered, but the best fitting was observed when both orders with respect to each reactant and both stoichiometric coefficients were unity.

Acknowledgements

F. D. is a grateful recipient of a fellowship from the National Research Council (Conicet). The courtesy of the Department of Physical Chemistry of the *Universidad de Mar del Plata* where the EPR measurements were carried out, is acknowledged. The authors are indebted to the CONICET and the University of Buenos Aires for financial support.

References

1 (*a*) E. C. Ashby, *Acc. Chem. Res.*, 1988, **21**, 414; (*b*) E. C. Ashby and T. Pham, *J. Org. Chem.*, 1987, **52**, 1292; (*c*) E. C. Ashby, D. Coleman and M. Gamasa, *J. Org. Chem.*, 1987, **52**, 4079.

2 (*a*) H. Yamataka, N. Fujimura, Y. Kawafuji and T. Hanafusa, *J. Am. Chem. Soc.*, 1987, **109**, 4305; (*b*) H. Yamataka, T. Matsuyama and T. Hanafusa, *Chem. Lett.*, 1987, 647; (*c*) T. Matsuyama, H. Yamataka and T. Hanafusa, *Chem. Lett.*, 1988, 1367.

3 (*a*) A. G. Neville, C. E. Brown, D. M. Rayner, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1991, **113**, 1869; (*b*) A. J. Reich, D. P. Green and N. H. Phillips, *J. Am. Chem. Soc.*, 1989, **111**, 3444.

4 (*a*) K. Maruyama and T. Katagiri, *J. Phys. Org. Chem.*, 1991, **4**, 381; (*b*) K. Maruyama and T. Katagiri, *J. Phys. Org. Chem.*, 1991, **4**, 158 and refs. therein.

5 (*a*) H. Yamataka, N. Miyano and T. Hanafusa, *J. Org. Chem.*, 1991, **56**, 2573.

6 N. S. Nudelman, Carbonylation of Main-Group Organometal Compounds, in *The Chemistry of Double Bonded Functional Groups*, eds. S. Patai and Z. Rappoport, ch. 13, Wiley, Chichester, 1989.

7 D. Seyferth, R. C. Hui, R. M. Weinstein and W.-L. Wang, *Nova Acta Leopold.*, 1985, **9**, 335 and refs. therein.

8 (*a*) A. A. Vitale, F. Doctorovich and N. S. Nudelman, *J. Organomet. Chem.*, 1987, **332**, 9; (*b*) N. S. Nudelman and A. A. Vitale, *J. Org. Chem.*, 1981, **46**, 4625; (*c*) N. S. Nudelman and A. A. Vitale, *J. Organomet. Chem.*, 1983, **241**, 143; (*d*) N. S. Nudelman and A. A. Vitale, *Org. Prep. Proced. Int.*, 1981, **13**, 144.

9 (*a*) N. S. Nudelman, E. S. Lewkowicz and J. P. J. Furlong, *J. Org. Chem.*, 1993, **58**, 1847; (*b*) N. S. Nudelman, E. S. Lewkowicz and D. G. Perez, *Synthesis*, 1990, 917; (*c*) D. G. Perez and N. S. Nudelman, *J. Org. Chem.*, 1988, **53**, 408.

10 L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. S. Nudelman and G. M. Whitesides, *J. Am. Chem. Soc.*, 1973, **95**, 8118.

11 N. S. Nudelman, F. Doctorovich and G. Amorin, *Tetrahedron Lett.*, 1990, **31**, 2533.

12 (*a*) M.-A. Fox, *Chem. Rev.*, 1992, **92**, 365; (*b*) L. Eberson, *New J. Chem.*, 1992, **16**, 151; (*c*) *Electron Transfer in Inorganic, Organic and Biological Systems*, eds. J. R. Bolton, N. Mataga and G. McLendon, Adv. Chem. Ser. 228, ACS, Washington, DC, 1991; (*c*) J. M. Saveant, *New J. Chem.*, 1992, **16**, 131; (*d*) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, Berlin, Heidelberg, 1987; (*e*) *Photoinduced Electron Transfer*, eds. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988.

13 S. F. Rak and L. L. Miller, *J. Am. Chem. Soc.*, 1992, **114**, 1388.

14 A. Loupy, B. Tchoubar and D. Astruc, *Chem. Rev.*, 1992, **92**, 1141.

15 J. M. Savéant, *New J. Chem.*, 1992, **16**, 131.

16 L. Eberson, B. Olofsson and J. O. Svensson, *Acta Chem. Scand.*, 1992, **46**, 1005.

17 B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon, Oxford, 1974.

18 A. Maercker, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 972.

19 C. G. Screttas and B. R. Steele, *J. Org. Chem.*, 1989, **54**, 1013.

20 N. S. Nudelman, M. Marder and A. Gurevich, *J. Chem. Soc., Perkin Trans. 2*, 1993, 229.

21 B. J. Wakefield, in *Comprehensive Organic Chemistry*, eds. D. Barton and W. D. Olli, Pergamon, Oxford, 1979, vol. 3, p. 943ff.

22 C. G. Screttas and M. Micha-Screttas, *J. Phys. Chem.*, 1983, **87**, 3844.

23 H. Joela, *Comput. Chem.*, 1987, **12**, 189.

24 M. Iwazumi, M. Suzuki, T. Isobe and H. Azumi, *J. Phys. Chem.*, 1968, **41**, 732.

25 N. S. Nudelman and P. Outumuro, *J. Org. Chem.*, 1982, **42**, 4347.

26 F. Doctorovich and N. S. Nudelman, *Magn. Reson. Chem.*, 1990, **28**, 576.

27 N. S. Nudelman and F. Doctorovich, *Tetrahedron*, 1994, in press.

28 *Solubility Data Series, Carbon Monoxide*, ed. R. W. Cargill, Pergamon, Oxford, New York, 1990.

29 P. J. Hanhela and D. B. Paul, *Aust. J. Chem.*, 1970, **34**, 1701.

30 H. W. Moore, Y. L. Sing and R. S. Sidhu, *J. Org. Chem.*, 1977, **42**, 3320.

31 W. Buchner, *Chem. Ber.*, 1966, **99**, 1485.

32 (*a*) N. Rizkallc and A. Goliaszewski, *ACS Symp. Ser.*, 1987, **328**, 136; (*b*) E. Prent, *ACS Symp. Ser.*, 1987, **328**, 154.

33 G. R. Stevenson and R. T. Hashim, *J. Am. Chem. Soc.*, 1985, **107**, 5794.

34 (*a*) E. C. Ashby and J. N. Argyropoulos, *J. Org. Chem.*, 1986, **51**, 472; (*b*) R. N. Ashby, R. N. De Priest and W.-Y. Su, *Organometallics*, 1984, 1718.

35 (*a*) H. Yamataka, *J. Phys. Org. Chem.*, 1992; (*b*) H. Yamataka, Y. Kawafuji, K. Nagareda, N. Miyano and T. Hanafusa, *J. Org. Chem.*, 1989, **54**, 4706.

36 T. Hiiro, Y. Morita, T. Inoue, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Am. Chem. Soc.*, 1990, **112**, 455.

37 (*a*) J. D. Protasiewicz and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 6564; (*b*) V. Dufaud, B. J.-M. Thivolle-Cazat, R. Mathieu, J. Jaud, J. Brower and D. C. Waissermann, *J. Am. Chem. Soc.*, 1983, **105**, 146.

38 C. Walling, *J. Am. Chem. Soc.*, 1988, **110**, 6845.

39 J. C. Scaiano and L. C. Stewart, *J. Am. Chem. Soc.*, 1983, **105**, 3609.

40 A. Bakac and J. H. Espenson, *J. Chem. Soc., Chem. Commun.*, 1991, 1497.

41 G. T. Mondodoev, N. M. Przhiyalgouskaya and V. N. Belov, *Zh. Org. Khim.*, 1965, **1**, 2008.

42 J. Schmidlin and P. Massini, *Ber. Dtsch. Chem. Ges.*, 1909, **42**, 2388.

43 D. F. Shriver, *The Manipulation of Air Sensitive Compounds*, Wiley, New York, 1989.

Paper 4/00303I
Received 18*th January* 1994
Accepted 1*st March* 1994