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Thermal decomposition of cobalt carbonyl complexes in viscous media ☆

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Abstract

The thermal decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and further to metallic cobalt and CO under an inert atmosphere at temperatures <90 °C in hydrocarbon solutions and in the solid state have been studied and are documented in the literature. The mechanistic aspects of the solid state decomposition were similar to those found with the solution decomposition, but the kinetic aspects were quite different, since the rate constant, k_{obs}, found for the solid state reaction, was two orders of magnitude lower than the one found for the solution reaction. The decomposition reaction of cobalt carbonyls is primarily governed by diffusion. The diffusion of the cobalt carbonyls through a certain medium is strongly dependent on the viscosity of that medium. In a solution containing a polymeric system, the viscosity is a dominant property, since it is directly proportional to the concentration of the polymer in the solution. Therefore, the solution and solid state decompositions may be viewed as two extreme cases, in which the only variable is the viscosity of the polymeric solution. In the solution case, in the absence of polystyrene, the viscosity of the solution is essentially the viscosity of pure hydrocarbon solvent (toluene), while in the solid state case, the viscosity of the composite polystyrene film (the film containing the cobalt carbonyl complex) may be approximated as the viscosity of solid polystyrene just before its melting point. There are no studies to date which examine the effect of the viscosity of the solution of the cobalt carbonyl complexes on their thermal decomposition reaction in an inert atmosphere. Therefore, a study of the variation of the rate constants of the decomposition reactions as a function of the concentration of the polystyrene component in the cobalt carbonyl toluene solutions was undertaken. The reaction rates decreased with increasing polystyrene concentration, but only after a critical polymer concentration, c^*, which is the coil overlap concentration, was reached. The data obtained are reported here with conclusions concerning the mechanism of the thermal decomposition reaction of cobalt carbonyl complexes to produce zero-valent cobalt particles.

Keywords: Kinetics and mechanism; Thermal decomposition; Cobalt complexes; Carbonyl complexes

1. Introduction

Thermolysis of transition metal carbonyl complexes in solution under an inert atmosphere is a well known technique for the preparation of pure metal powders [1,2]. The thermal decomposition of $Co_2(CO)_8$ in hydrocarbon solutions to $Co_4(CO)_{12}$ and further to metallic cobalt and carbon monoxide under an inert atmosphere has been extensively studied and is well documented in the literature [3–10]. At temperatures <90 °C, the decomposition proceeds in two steps: the first step consists of the solution equilibrium decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ with the release of CO (gas) and the second step consists of the irreversible decomposition of $Co_4(CO)_{12}$ to Co^0 clusters and the release of CO (gas).

$$2Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + 4CO\uparrow \qquad (1)$$

$$Co_4(CO)_{12} \longrightarrow 4Co + 12CO\uparrow \qquad (2)$$

The first reaction (in solution) has generated substantial interest since several studies have yielded contradictory results: in heptane, reaction (1) is assigned either second-order [3,4] or a fractional order [5], whereas in toluene first-order [6] or second-order [7,8] have been considered. The inverse reaction of (1) shows the importance of the partial pressure of carbon mon-

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☆ This paper is dedicated to Professor György Bor on the occasion of his 70th birthday, in honor of his outstanding contributions to organometallic chemistry and his tireless struggle for a free society in his homeland.

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oxide, which inhibits the decomposition of $Co_2(CO)_8$. The contribution of P_{CO} to the rate equation of reaction (1) has been observed to vary between second to fourth inverse powers [9].

The second reaction (2) has not drawn great interest, and only two publications mention it in connection with the inhibiting effect of carbon monoxide [6,10]. However, Bor et al., in their classical diagram of the stability regions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ as a function of temperature and CO partial pressure [9], show that at temperatures above 90 °C and $P_{CO} < 0.1$ atm (in inert atmosphere), the cobalt carbonyls will decompose to metallic cobalt and carbon monoxide.

The thermal decomposition reaction of cobalt carbonyl complexes was also studied in the solid state [11]. The $Co_2(CO)_8$ compound was dispersed in a polymeric matrix, the solvent was removed, and the resulting films were exposed to thermal radiation under controlled N_2 or Ar atmospheric conditions. The mechanistic aspects of the solid state decomposition were similar to those found with the solution decomposition, as concluded from the type of intermediates formed in the reaction in both cases and from the nature of the end-products. It is not clear, however, to what degree (if at all) the polymeric matrix is involved in the reaction mechanism. It was previously reported that the molecular weight of polystyrene was not affected by the thermal decomposition reaction [11,12], and the network degraded by less than 10% (which is within the experimental error for the calculations of molecular weight from viscosity measurements). The kinetic aspects, however, were quite different, since the rate constant, k_{obs} found for the solid state reaction, was two orders of magnitude smaller than the one found for the solution reaction (-5.27×10^{-6} and -6.38×10^{-4} l mol^{-1} s^{-1}, respectively) [11]. Hence, embedding $Co_2(CO)_8$ in a polymeric matrix (high molecular weight polystyrene) significantly slowed down the decomposition process. Since the decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and further to metallic Co is primarily governed by diffusion, it is very reasonable to assume that in the solid state polystyrene system, a considerable slowing of diffusion of $Co_2(CO)_8$ through the matrix occurs, thus giving rise to lower reaction rates.

The diffusion of a molecule through a certain medium is strongly dependent on three factors: the mobility of the molecule, the temperature, and the viscosity of the medium [13]. In a solution containing a polymeric system, the viscosity is a dominant property, since it is directly proportional to the molecular weight of the polymer and to the concentration of the polymer in the solution. The dependence on concentration, however, is quite complex [14–18]. Below a certain critical concentration in solution, the dilute regime, the polymer chains are well isolated, each having a well defined excluded volume, and the viscosity is proportional to the concentration. Above the critical concentration in solution, the semi-dilute or concentrated regimes, the polymer chains become entangled with each other since they now penetrate into each other's excluded volume space, and the viscosity is non-linearly dependent on concentration.

Therefore, the solution and solid state decompositions may be viewed as two extreme cases, in which the molecular weight of the polystyrene and the temperature of decomposition are fixed parameters and the only variable is the viscosity of the polymeric solution. In the solution case, in the absence of polystyrene, the viscosity of the solution is essentially the viscosity of pure toluene, while in the solid state case, the viscosity of the composite polystyrene film (the film containing the cobalt carbonyl complex) may be approximated as the viscosity of a polystyrene melt. Studies by Hess and Parker [19] and Horny [20] describe stabilization of colloidal cobalt particles in dilute polymer solutions, by adsorption of the polymer to the metal particles to form a film that separates the particles sufficiently to keep van der Waals forces below thermal energy levels. There are no studies to date which examine the effect of the viscosity of the solution of the cobalt carbonyl complexes on their thermal decomposition reaction in an inert atmosphere. If the polymer plays no role in this decomposition reaction except increasing the viscosity of the solution, then one expects to observe a linear decrease in rate constants with an increase in polystyrene concentration in solution, due mainly to diffusional slow-down effects. If, on the other hand, the polymer plays an active role in the decomposition reaction, then the dependence of the rate constants on polystyrene concentration will not be linear. Therefore, a study of the variation of the rate constants of reactions (1) and (2) as a function of the concentration of the polystyrene moiety in the cobalt carbonyl solutions was undertaken. The data obtained are reported here with conclusions concerning the mechanism of the thermal decomposition reaction of cobalt carbonyl complexes to produce zero-valent cobalt particles.

2. Results and discussion

2.1. *Quantitative infrared spectroscopic measurements*

The identification of cobalt carbonyl species in solution or in a solid polymer matrix, as well as quantitative determination of cobalt carbonyl concentrations in solution and in the polymer matrix was carried out by IR spectroscopy. The carbonyl absorption bands of cobalt carbonyls, both terminal and bridging, are very sharp and well contoured in the 1800–2200 cm^{-1} region [21–23] and permit an accurate evaluation of concentration, without solvent spectral interference (which can be eliminated in any case by proper spectral manipulations).

The IR spectra of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in a toluene solution are shown in Fig. 1. There are two main absorption regions of interest: (a) the absorption bands in the region between 2020 and 2070 cm^{-1}, which correspond to the terminal CO groups in both complexes [24–27], (b) the 1858 and 1867 cm^{-1} absorption bands which correspond to the bridging CO groups both in $Co_2(CO)_8$ and $Co_4(CO)_{12}$ [24–27]. The two main absorption regions are retained also in the IR spectra of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in a polystyrene matrix, but some significant changes occur and they are shown in Fig. 2. There is a general broadening of the spectrum of $Co_2(CO)_8$, that results in the formation of only two terminal carbonyl bands of approximately equal intensity at 2030 and 2065 cm^{-1} and only one bridging carbonyl band at 1858 cm^{-1}. The same broadening of the spectrum in the solid state is observed also in the spectrum of $Co_4(CO)_{12}$, resulting in the formation of only one terminal carbonyl band at 2058 cm^{-1}, with the preservation of the bridging carbonyl band at 1867 cm^{-1}. The effect of the incorporation of the cobalt carbonyls into the polystyrene matrix is much more evident with the terminal carbonyl bands than with the bridging carbonyl bands. This is probably due to a lessening of the number of degrees of freedom for the vibrations of the terminal carbonyls in the solid state, while the vibrations of the bridging carbonyls are relatively more restricted both in solution and in the solid state.

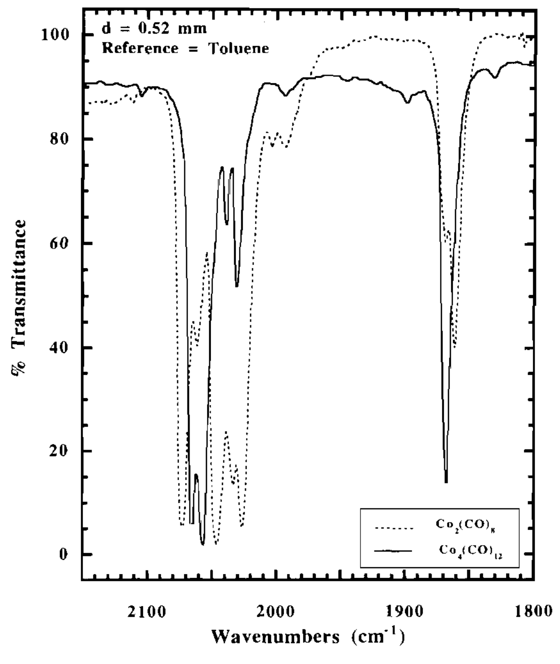

Fig. 1. IR spectra of a 4.76×10^{-2} M solution of $Co_2(CO)_8$ (– – –) and a 4.51×10^{-2} M solution of $Co_4(CO)_{12}$ (——) in pure toluene.

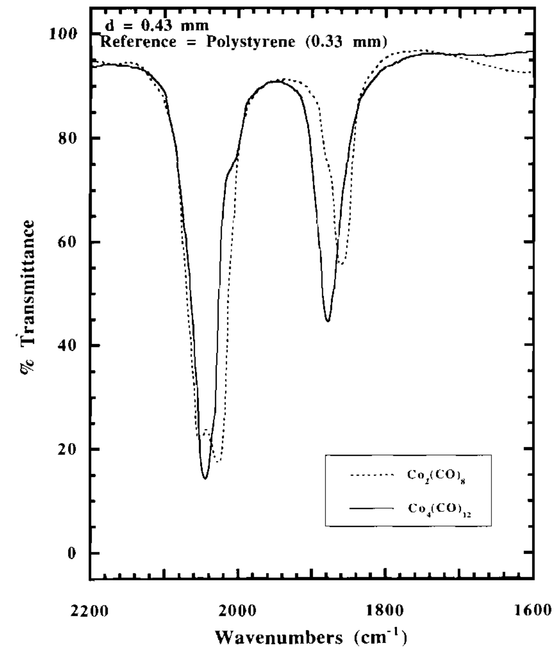

Fig. 2. IR spectra of 30 wt.% $Co_2(CO)_8$ (– – –) and 30 wt.% $Co_4(CO)_{12}$ (——) in a polystyrene film cast from a polystyrene–toluene solution by the method described previously [11].

The quantitative analysis of carbonyl concentration was based upon the intensity variations of the 1858 and 1867 cm^{-1} bands. The bridging region was chosen as the analytical reference for the following reasons. (i) $Co_2(CO)_8$ is a mixture of three isomers whose relative concentrations are dependent upon temperature, pressure and reaction conditions [28]. Two of these isomers do not have bridging carbonyls, and hence the 1858 cm^{-1} band belongs only to the bridging isomer. Therefore, changes in the intensities of the terminal carbonyl bands would not necessarily reflect changes in the absolute concentration of $Co_2(CO)_8$, but may indicate changes in the relative concentrations of the three isomers. On the other hand, the concentration of the bridging isomer is known for every temperature [28], and changes in the 1858 cm^{-1} band may be directly correlated to the absolute concentration of $Co_2(CO)_8$ [20]. (ii) The spectrum of the terminal carbonyl region for a mixture of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ is much too complex for an effective quantitative analysis. On the other hand, $Co_4(CO)_{12}$ has a bridged structure exclusively, and therefore, changes in the intensity of its 1867 cm^{-1} band reflects changes in its absolute concentration. (iii) The general broadening of the spectrum causes overlap of some of the bands in the terminal carbonyl region, and hence these bands cannot be used for analytical purposes. The 1858 and 1867 cm^{-1} bands, on the other hand, are isolated bands, and even though they are considerably broader in the solid state, they can still be used for quantitative analysis.

A crucial element of the quantitative analysis of the cobalt carbonyl mixture is the determination of the adequate molar absorption extinction coefficients for the 1858 and 1867 cm^{-1} bands. Some extinction coefficient values for the bridging carbonyl IR absorption bands of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in hydrocarbon solvents have been reported in the literature [21,29,30]. For dilute solutions, $\sim 10^{-1}$–10^{-3} M, these values are:

for $Co_2(CO)_8$: $\epsilon_{1858} = 1954$ l mol^{-1} cm^{-1}

for $Co_4(CO)_{12}$: $\epsilon_{1867} = 10440$ l mol^{-1} cm^{-1}

In the solid state case [11], i.e. when $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are embedded in a polymeric matrix such as polystyrene to form solid films of 0.5–0.8 mm in thickness, the extinction coefficient values were by two orders of magnitude lower than in solution. For concentrations of cobalt carbonyls in the films of 10–30 wt.%, these values are:

for $Co_2(CO)_8$: $\epsilon_{1858} = 84$ l mol^{-1} cm^{-1}

for $Co_4(CO)_{12}$: $\epsilon_{1867} = 795$ l mol^{-1} cm^{-1}

It is very likely that the solid state imposes some restrictions on the free movement of the carbonyl groups of both $Co_2(CO)_8$ and $Co_4(CO)_{12}$, which results in the considerable lowering of the extinction coefficients of both complexes [11] The same phenomenon has also been observed with other carbonyl complexes [12].

Since the main thrust of this study is to understand the influence of solution viscosity on the kinetics and mechanism of the carbonyl decomposition process, reactions (1) and (2), it was important to determine the values of the extinction coefficients of the 1858 and 1867 cm^{-1} bands in solutions of increasing viscosities. Fig. 3 shows the variation of the extinction coefficients of the 1858 and 1867 cm^{-1} bands as a function of the concentration (expressed in wt.%) of polystyrene present in the solution. For dilute polystyrene solutions, up to 1 wt.%, the extinction coefficients of the 1858 and 1867 cm^{-1} bands are similar to the pure hydrocarbon solution without the polymer. The largest variation is observed for the semi-dilute regime, 2–20 wt.% of polystyrene. The rate of the decrease for ϵ_{1858} is -112.08 l mol^{-1} cm^{-1} (wt.%)$^{-1}$, and for ϵ_{1867} it is -376.85 l mol^{-1} cm^{-1} (wt.%)$^{-1}$. Beyond the semi-dilute regime, for polystyrene concentrations of 20–60 wt.%, the rate of decrease for ϵ_{1858} and ϵ_{1867} is smaller, and for polystyrene concentrations >60 wt.%, the solution viscosity changes minimally with additional increase in polystyrene concentration.

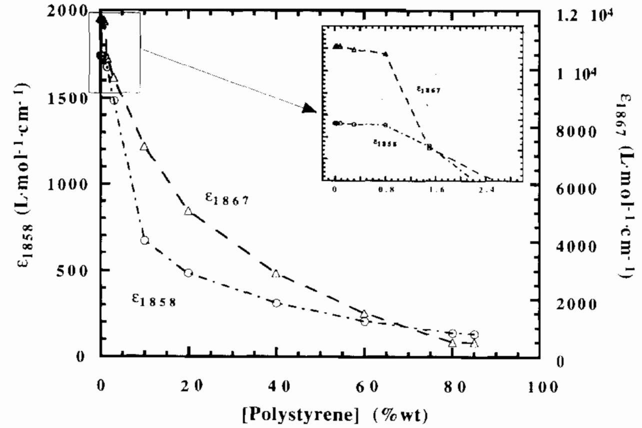

Fig. 3. Variation of the extinction coefficients of the 1858 and 1867 cm^{-1} bands as a function of the concentration of polystyrene in solution (expressed as wt.%). The gray insert is a blow-up of the region of very dilute polystyrene solutions, $0 < [PS] < 3$ wt.%, where ϵ_{1858} and ϵ_{1867} are unchanged.

2.2. *Thermal decomposition of the cobalt carbonyl complexes*

The thermal decomposition process of $Co_2(CO)_8$ in inert atmosphere to produce zero-valent cobalt particles consists of two reactions. Reaction (1) is an equilibrium reaction with k_f as the rate constant of the forward reaction and k_r as the rate constant of the reverse reaction. Reaction (2) is irreversible with k_3 as its rate constant. Since the resulting CO released during the reaction is removed by the constant flushing of the reaction mixture with N_2, it is reasonable, as a first approximation, to assume that the reverse reaction in reaction (1) is negligible, and therefore the rate constant for the second-order reaction becomes k_{obs} and the rate expression is:

$$\frac{-2x}{a(a-2x)} = k_{obs}t \qquad (3)$$

(where $a = [Co_2(CO)_8]_{t=0}$ and $x = [Co_4(CO)_{12}]_t$).

Reaction (2) may be approximated to be a first-order reaction, and therefore the rate constant becomes k_{dec} and the rate expression is:

$$\ln x = k_{dec}t \qquad (4)$$

(where $x = [Co_4(CO)_{12}]_t$).

If both reactions have rate constants of the same order of magnitude, the overall rate expression becomes very complicated. If on the other hand, reaction (1) or reaction (2) is the rate limiting step, i.e. either $k_{obs} \gg k_{dec}$ or $k_{obs} \ll k_{dec}$, then the overall rate expression would be simplified. Figs. 4 and 5 show typical IR spectra of both components of the overall decomposition reaction. In pure hydrocarbon solution (Fig. 4), the overall cobalt carbonyl material balance is kept intact due to the slowness of reaction (2), and therefore only the $Co_2(CO)_8 \rightarrow Co_4(CO)_{12}$ transformation is observed within the time allotted ($\sim$10 h). In the solid state (Fig. 5), since the rates of both reactions (1) and (2) are comparable, only a partial conversion of $Co_2(CO)_8$ into $Co_4(CO)_{12}$ is observed, and after $\sim$48 h, a general decrease in carbonyl concentration, of both $Co_2(CO)_8$ and $Co_4(CO)_{12}$, occurs.

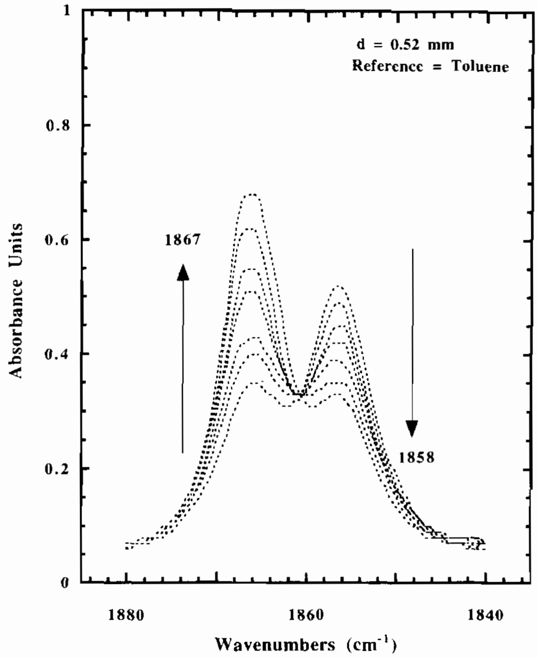

Fig. 4. Typical IR spectra of the composite effect of reaction (1) and reaction (2) in pure hydrocarbon solvent. Due to the slowness of reaction (2), only the $Co_2(CO)_8 \rightarrow Co_4(CO)_{12}$ transformation is observed.

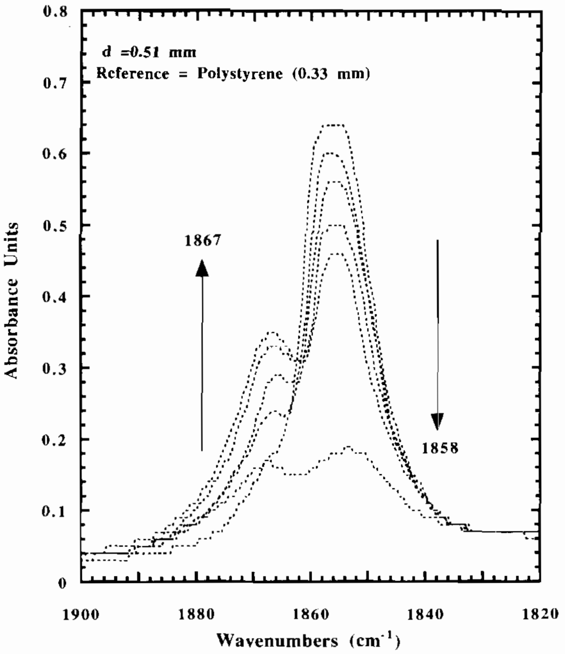

Fig. 5. Typical IR spectra of the composite effect of reaction (1) and reaction (2) in a polystyrene solid state film. Only a partial $Co_2(CO)_8 \rightarrow Co_4(CO)_{12}$ conversion is observed due to comparable k values.

Figs. 6 and 7 portray a comparison between the kinetics of reactions (1) and (2) in solution (Fig. 6) and in the solid state (Fig. 7) by plotting the left-hand side of Eqs. (3) and (4) as a function of time. The rate constants calculated for reactions (1) and (2), k_{obs}

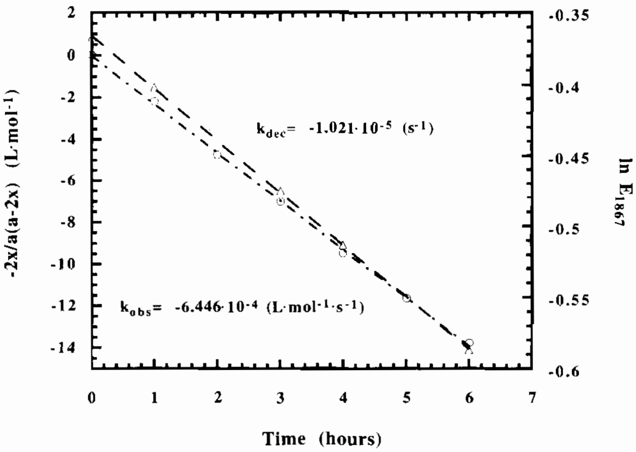

Fig. 6. Comparison of the kinetics of reactions (1) $(-2x/a(a-2x)$ vs. $t)$ and (2) ($\ln x$ vs. t), in pure toluene solution.

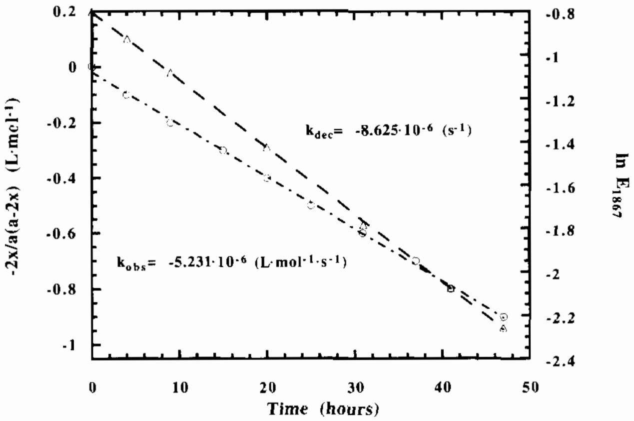

Fig. 7. Comparison of the kinetics of reactions (1) $(-2x/a(a-2x)$ vs. $t)$ and (2) ($\ln x$ vs. t), in a solid polystyrene film.

and k_{dec}, in hydrocarbon solution and in the solid state, are:

in hydrocarbon solution:

$k_{obs(HC)} = -6.446 \times 10^{-4}\ l\ mol^{-1}\ s^{-1}$

$k_{dec(HC)} = -1.021 \times 10^{-5}\ s^{-1}$

in the solid state:

$k_{obs(SS)} = -5.231 \times 10^{-6}\ l\ mol^{-1}\ s^{-1}$

$k_{dec(SS)} = -8.625 \times 10^{-6}\ s^{-1}$

In pure hydrocarbon solutions, the decomposition reaction of $Co_4(CO)_{12}$ to Co^0 is the rate limiting step and therefore the overall reaction rate may be approximated to be $|k_{dec}x|$. In the solid state, the decomposition reaction of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ is essentially the rate limiting step and therefore the overall reaction rate may be approximated to be $|k_{obs}(a-2x)^2|$. However, the rates of both reactions decrease (reaction (1) by two orders ot magnitude), but the rate of the decomposition of $Co_4(CO)_{12}$ to metallic cobalt particles decreases more slowly, and it becomes of the same order of magnitude of the rate of reaction (1). The decrease of the rates of reactions (1) and (2) at a different pace indicates that these two reactions have different mechanisms, and therefore they are affected differently by the increase of the viscosity of the solutions in which these reactions are conducted.

As previously stated, the solution case and the polymeric film case are the two extreme situations, in which the same set of reactions are conducted in the liquid phase and in the solid state, respectively. In the liquid phase, since the solvent is a hydrocarbon solvent (toluene), the viscosity of the medium is small, and hence the diffusion of the cobalt molecules to form $Co_4(CO)_{12}$ in the first reaction and Co^0 particles in the second reaction is not restricted (it may be dependent on the rate of stirring of the reaction mixture). As polystyrene is added to the solution, the viscosity increases, and therefore it is expected that the diffusion-dependent reaction rates will decrease accordingly, until they will reach the values measured for the solid state case. Fig. 8 shows a plot of the various k_{obs} and k_{dec} values measured and calculated for a series of polystyrene-containing solutions with an increasing polystyrene content. At low polystyrene concentration, $[PS] < 0.1$ wt.%, k_{obs} remains unchanged, followed by a constant decrease for the region 0.1 wt.% $< [PS] < 20$ wt.%, and a new plateau for $[PS] > 20$ wt.% at a value which is two orders of magnitude lower than the k_{obs} in a pure solvent. The behavior of k_{dec}, on the other hand, proves to be somewhat unexpected. For $[PS] < 0.1$ wt.%, k_{dec} remains unchanged, but immediately thereafter, for the region 0.1 wt.% $< [PS] < 3$ wt.%, k_{dec} increases sharply, to reach its highest value, $k_{dec(max)} = -4.882 \times 10^{-5}$ s^{-1} at $[PS] = 1.5$ wt.%. For $[PS] > 3$ wt.%, the rate decreases and stabilizes at a value which is half an order of magnitude lower than k_{dec} in pure solvent.

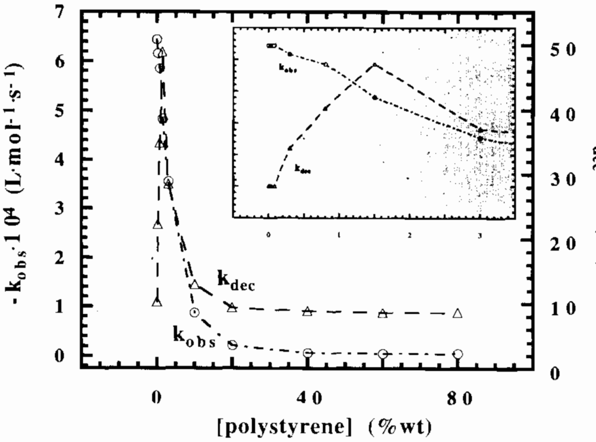

Fig. 8. The variation of k_{obs} and k_{dec} as a function of the concentration of polystyrene in solution (expressed as wt.%). The gray insert is a blow-up of the region of very dilute polystyrene solutions, $0 < [PS] < 3$ wt.%, where the behavior of k_{obs} and k_{dec} is very different.

A closer examination of the polystyrene solution for which k_{dec} reaches its maximal value reveals that the polystyrene content corresponds to its critical concentration in dilute solutions, c^*, a concentration which marks the onset of the coil overlap process between the polymer chains in solution, also known as *entanglement* [18,29–31]. Hence, for polystyrene concentrations $[PS] < c^*$, the polymer coils have infinite dilution radii and do not overlap, while for $[PS] = c^*$, the coils begin to overlap having reached the overlap threshold. At this critical concentration c^*, the intrinsic viscosity, $[\eta]$, corresponds to the relationship: $c^*[\eta] = 1$ [18]. The intrinsic viscosity is a measure of the polymer's ability to increase solution viscosity in the absence of intermolecular effects, i.e. at infinite dilution. The intrinsic viscosity of polystyrene in toluene may be calculated according to the Mark–Houwink experimental relation: $[\eta] = KM^a$, where K and a are specific constants for various polymer/solvent combinations [32]. For an average molecular weight of 250 000 for the polystyrene which was used throughout this experiment, $[\eta] = 9.016 \times 10^{-2}$ l g^{-1}, and correspondingly, $c^* = 11.091$ g l^{-1}, or $c^* = 4.436 \times 10^{-5}$ (mol l^{-1}), or $c^* = \sim 1.5$ wt.%.

The behavior of k_{dec} as a function of polystyrene concentration in solution suggests that for $[PS] < 1.5$ wt.%, i.e. $[PS] < c^*$, the presence of polystyrene has a catalytic effect on the decomposition of $Co_4(CO)_{12}$ to Co^0. The mechanism of cluster formation, which was collectively referred to as reaction (2), may be described in the following way:

Cluster stepwise growth:

$$Co_j + Co_1 \longrightarrow Co_{j+1} \quad (5)$$

Cluster aggregation:

$$Co_j + Co_k \longrightarrow Co_{j+k} \quad (6)$$

Cluster dissociation:

$$Co_k \longrightarrow Co_i + Co_j \quad (7)$$

The study of nucleation, growth and coagulation of metal particles is a distinct area of the materials science discipline, and the theories involved shall not be discussed here. However, it should be noted that most of these reactions occur in colloidal suspensions and are therefore solid state reactions in nature [33–35]. These types of colloidal reactions are strongly enhanced by the presence of large macromolecules in the suspension, which provide the solid state support necessary for the propagation of the cluster growth or aggregation. In the dilute regime of reaction (2), when the polystyrene concentration is below the coil overlap threshold, the polymer chains have infinite dilution radii and can provide the necessary support for the growth and aggregation reactions of the cobalt particles. On the other hand, the viscosity of the dilute solution is practically identical to that of the pure toluene solvent, and hence the mobility of the molecules is not hindered by the presence of the polymer. This is also supported by the behavior of k_{obs} in reaction (1), which remains essentially constant for $[PS] < c^*$. For $[PS] > c^*$, the diffusional slow-down effects created by the formation of entanglements in the polymer present in solution reduce the reaction rates for all reactions in the system, i.e. reactions (1) and (2), where reaction (2) is the overall reaction resulting from (5), (6) and (7).

Additional experimental information comes from the analysis of the molecular weight of the polystyrene moiety in solution. Previously, we reported that when decomposition reactions were carried out in the polystyrene solid state films [11], the viscosity average molecular weight of the polystyrene matrix decreased by less than 10%, which is within the uncertainty connected with this type of measurement. In the experiments described here, all polystyrene solutions were analysed after the decomposition reactions were completed, and the viscosity average molecular weights that were calculated ranged between 252 000 and 229 500. This provides additional support for the fact that there was no chemical interaction between the polystyrene and the cobalt complexes and particles, and the polystyrene molecules below c^* acted as a solid state support.

Table 1
The preparation of polystyrene solutions of various concentrations (and hence various viscosities) to be used in the experiment

Solution	Toluene (ml)	Polystyrene (g)	[Polystyrene]	
			(mol l^{-1}×10^{6})	(wt.%)
a	250	0.065	1.04	0.03
b	250	0.108	1.73	0.05
c	250	0.173	2.76	0.08
d	250	0.216	3.45	0.10
e	250	0.324	5.18	0.15
f	250	0.648	10.40	0.30
g	250	1.083	17.30	0.50
h	250	1.731	27.60	0.80
i	250	2.160	34.50	1.00
j	250	3.240	51.80	1.50
k	250	6.480	104.00	3.00
l	250	21.600	345.00	10.00
m	250	43.200	690.00	20.00
n	250	86.400	1380.00	40.00
o	250	129.600	2070.00	60.00
p	250	172.800	2760.00	80.00
q	250	183.600	2932.50	85.00

3. Experimental

3.1. Preparation of polystyrene solutions

3.24 g of polystyrene (Aldrich Chemicals, *MW*(av.) = 250 000, powder form) were dissolved in 250 ml toluene (Fluka Chemical Corp., USA, b.p. 110 °C, $d = 0.867$), to produce a 0.518×10^{-4} M solution corresponding to its critical concentration c^* of ~1.5 wt.%. Other solutions, a–q, are listed in Table 1. The toluene used in these solutions was dried by molecular sieve pellets (Matheson, Coleman and Bell) and redistilled under N_2 stream. The solutions were mixed in a 500 ml round-bottom flask for 24 h at room temperature. The more concentrated solutions (polystyrene concentrations above 40 wt.%) were refluxed under N_2 at 90–100 °C to ensure homogeneity. All solutions were either used immediately or stored under a nitrogen atmosphere.

3.2. Decomposition of cobalt carbonyl solutions

The solution decomposition of $Co_2(CO)_8$ in an inert atmosphere, reaction (1), was performed by the classical method of Natta et al. [7]. A solution of 0.8 g $Co_2(CO)_8$ (Johnson Matthey/Alfa Products) in 50 ml toluene (Fluka Chemical Corp., $d = 0.867$), corresponding to a concentration of 4.76×10^{-2} M, was prepared in a 100 ml three-neck round-bottomed flask flushed with carbon monoxide. The middle neck was equipped with a reflux condenser, a side neck with a rubber stopper and the other neck with a thermometer. The rubber outlet was also used for sampling. The reflux condenser was equipped with a gas inlet–outlet glass fitting device. The outlet part was connected to a tube whose other side was inserted securely into the vent. These special precautions had to be taken in order to flush away carbon monoxide gas formed during both decomposition reactions. Then the flask was placed in a controlled heated oil bath, and the decomposition reaction carried out for approximately 10 h at 90 °C under a continuous N_2 stream. Stirring was essential throughout the reaction time. During the reaction period, samples were removed with a syringe at various time intervals, and their IR spectra recorded in NaCl liquid cells with toluene as a reference.

The solution decomposition of $Co_4(CO)_{12}$, reaction (2), was carried out in a similar apparatus. 1.287 g of freshly prepared $Co_4(CO)_{12}$ crystals [7] were dissolved in 50 ml toluene, corresponding to a 4.51×10^{-2} M solution. The reaction was carried out for approximately 48 h at 90 °C under a constant N_2 stream. Sampling was performed as described above.

The decomposition reactions performed in solutions containing polystyrene were identical to the procedure described so far, but instead of using pure toluene as the solvent, the polystyrene solutions a–q were used (Table 1), depending on the desired polymer concentration. For polystyrene solutions of 40 wt.% and above, some heating with vigorous stirring was necessary to ensure homogeneity of the solutions.

The values of the extinction coefficients for the 1858 and 1867 cm^{-1} bands in polymer solutions of increasing viscosity were obtained by recording the IR spectra of the polystyrene solutions a–q containing varying amounts of cobalt carbonyls, similarly to the method described elsewhere [36].

The solid state decompositions and extinction coefficient evaluation were performed using the techniques described in a previous publication [11]. Intrinsic viscosities $[\eta]$ of polystyrene and the cobalt–polystyrene compositions were determined using an Ubbelohde OB viscosimeter, and used to calculate *MW*(av.) of the polystyrene moieties.

3.3. *Infrared spectroscopic measurements*

IR spectra were recorded on an IBM-IR-44 Fourier transform spectrometer using a demountable liquid cell purchased from Crystal Laboratories, and equipped with a 0.5 mm spacer and new NaCl windows. The cell chamber was purged with dry nitrogen for at least half an hour before collecting interferograms. The resolution was 0.5 cm^{-1}, and 3000 scans were taken for both the sample and the reference solutions. The empty, clean and dry liquid cell was used as the background. Upon completion of each interferogram, the sample in the cell was removed by vacuum suction, and the cell thoroughly flushed with toluene. When samples contained viscous solutions (over 40 wt.% of polystyrene), the liquid cell was disassembled, the NaCl crystals and spacer were washed in toluene, and then the cell was reassembled using the same spacer. Spectral subtraction was performed using a subtraction factor of 1.00 in order to avoid possible spectral distortions.

4. Conclusions

In summary, since reaction (1) is primarily governed by diffusion, the reaction rate decreases with the increase in polystyrene content above the critical coil overlap concentration. Reaction (2), on the other hand, being a colloidal reaction, is greatly facilitated by the presence of the polymer, and the reaction rate increases considerably at polymer contents below and at the critical coil overlap concentration. Above this concentration, as the polymer coils become entangled and contracted, the decreased mobility of the molecules due to higher viscosity and lower diffusion rate has the effect of lowering the reaction rate of reaction (2) as well. The influence of the molecular weight of polystyrene on the reaction kinetics is now under investigation, since it can elucidate the mechanism of this 'catalytic' behavior.

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