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LETTER

Application of a Combined High-pressure Stopped-flow Photolysis Technique in Mechanistic Studies. The Thermal Ring-closure Reaction of Photochemically Produced $W(CO)_5$ (bipyridyl)

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The generation of organometallic intermediates via photolysis and the study of their reactivity has received significant attention from various groups in recent years [1–9]. Such studies could have important applications in the design of homogeneous catalytic processes. The mechanistic behaviour of such photo-generated intermediates is usually studied in terms of concentration and temperature dependences of the observed rate constants. Experience has shown that the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) usually reveal little mechanistic information, and in general much uncertainty exists in the interpretation of the $\Delta S^{\ddagger}$ data [1–3]. It is our experience that the application of pressure as a kinetic parameter can reveal very reliable mechanistic information and assist the assignment of the underlying reaction mechanism [10–12]. This has also been shown to be the case for the reactions of photochemically produced organometallic transients [13, 14].

In this paper we have studied the effect of pressure on the thermal ring-closure reaction of $W(CO)_5bpy$ (bpy = 2,2′-bipyridyl) produced as a transient during the photolysis of $W(CO)_6$ in the presence of bpy in toluene [2]. Since this reaction is too fast for conventional high-pressure techniques, it can be studied conveniently by irradiating a freshly mixed sample of the reaction components within the observation chamber of a high-pressure stopped-flow unit.

Experimental

$W(CO)_6$ (Riedel-de-Haen) was further purified by sublimation under vacuum. The ligand 2,2′-bipyridyl (Aldrich) was used without further purification. Toluene (Merck, uvasol) was refluxed over a Na/K alloy and distilled under nitrogen. Benzene (Merck, uvasol) was refluxed over Na and distilled under nitrogen. For some of the experiments the distilled benzene was purified further by absorptive filtration through Woelm basic alumina of activity grade 1 (ICN Pharmaceuticals Co., F.R.G.). Nitrogen used in the purging experiments was rigorously purified to remove H_2O and O_2, as described elsewhere [1].

The kinetics of the thermal ring-closure reaction was followed with the data-acquisition system [15] of the high-pressure stopped-flow unit [16]. For this purpose samples containing the required concentrations of $W(CO)_6$ and bpy were purged with N_2 for 15 min before filling the syringes of the stopped-flow unit. Following temperature and pressure equilibration, the components were mixed inside the stopped-flow unit and irradiated for 20 to 25 s with a 100 W Xe lamp through one of the windows in the high-pressure cell. The subsequent thermal ring-closure reaction was followed immediately after irradiation by rapidly connecting the detector light lead to the high-pressure cell and triggering the data-acquisition system. After completion of the reaction, the mixing system of the stopped-flow unit was activated to introduce a fresh mixture of reactants into the light path. This procedure could be repeated 40 times with one load of reagent solutions. The observed absorbance time plots at 514 nm (MLCT band of $W(CO)_4bpy$) exhibited good first-order behaviour for at least two to three half-lives of the reaction.

Results and Discussion

Irradiation of a mixture of $W(CO)_6$ and bpy rapidly produces $W(CO)_5bpy$, where bpy is coordinated in a monodentate fashion [1, 2]. This is followed by a slow thermal ring-closure reaction leading to the

$$W(CO)_6 + bpy \xrightarrow{h\nu} W(CO)_5bpy + CO \tag{1}$$

$$W(CO)_5bpy \xrightarrow{\Delta} W(CO)_4bpy + CO \tag{2}$$

tetracarbonyl complex (characterized by an MLCT band at 514 nm) and the release of CO as shown in eqn. (2). A typical absorbance time trace and corresponding first-order plot observed during this step are shown in Fig. 1. Spectral changes with clean isosbestic points for the thermal ring-closure reactions of photogenerated $W(CO)_5(4,4'\text{-}R_2bpy)$ and

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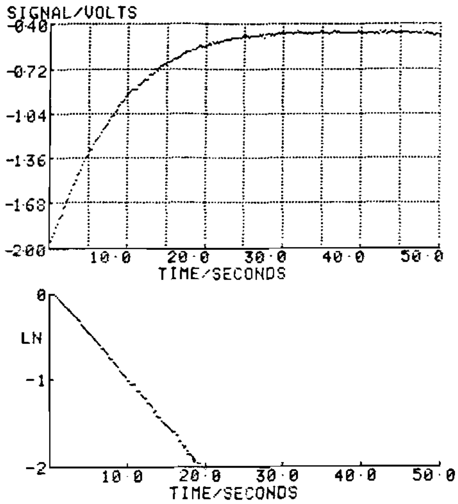

Fig. 1. A typical kinetic trace and corresponding first-order plot for the ring-closure reaction $W(CO)_5bpy \rightarrow W(CO)_4bpy + CO$ recorded at 50 MPa. For experimental conditions see Table 1.

$W(CO)_5bpy$ have been reported [1, 2] using FT-IR and diode-array spectroscopy. These observations lead us to believe that the thermal ring-closure of $W(CO)_5bpy$ is not complicated by any side or subsequent reaction and can therefore account for the good first-order behaviour observed in Fig. 1.

In some preliminary experiments, the reaction conditions were selected in agreement with those adopted by Lees *et al.* [1]. In benzene as solvent and for a specific set of reagents, the ring-closure reaction exhibited a meaningful dependence on the bipyridyl concentration. This is certainly not in accordance with that expected for a simple ring-closure reaction, which in principle should be independent of the ligand concentration. Possible explanations such as the participation of trace impurities that produce $W(CO)_5$(impurity) [1, 2] or the formation of a bridged complex of the type $(CO)_5W(\mu\text{-bpy})W(CO)_5$ as a possible intermediate, especially at low bpy concentrations [17], were considered. In later work, however, using fresh samples of all the chemicals involved, no significant concentration dependence was observed and no further attention was paid to this complication.

The pressure dependence of reaction (2) in benzene could only be studied over a limited pressure range because of the freezing of benzene at 70 MPa and 25 °C. The preliminary data indicated a volume of activation of -12 cm^3 mol^{-1} over the pressure range 5 to 50 MPa for 1:1 and 1:100 mixtures of $W(CO)_6$ and bpy at a $W(CO)_6$ concentration of 5×10^{-4} M. A more extended set of measurements were performed in toluene as solvent. The pressure and temperature dependences of this reaction were studied at a 1:15 mixture of $W(CO)_6$ and bpy, the results of which are summarized in Table 1.

The values of $\Delta V^{\ddagger}$, including the preliminary value for benzene as solvent, are significantly negative to support the operation of an associatively activated ring-closure process. The activation enthalpy for this step is also significantly lower than that reported for the dissociation of CO from hexacarbonyl complexes [18], which is most probably due to a strong *cis*-labilization effect of the ring-opened bpy ligand, combined with the latter's tendency to ring-close. The associative nature of the process is further supported by the significantly negative $\Delta S^{\ddagger}$ value found in this study. These results are in excellent agreement with data reported recently for the replacement of the S-bonded chelate ligands in $Mo(CO)_4(\widehat{SS})$ [19]. The reported $\Delta V^{\ddagger}$ values for the non-sterically hindered chelates vary between -9.3 and -11.3 cm^3 mol^{-1}, supporting the associative ligand substitution process. Similarly, $\Delta V^{\ddagger}$ values of -4.4, -12.2 and -14.9 were found for the substitution of $W(CO)_5THF$ by L, where L = piperidine, PPh_3 and $P(OEt)_3$, respectively [14], which support the associative nature of the process.

The results of the present study demonstrate how high-pressure stopped-flow and photolysis techniques can be combined to obtain mechanistic information

TABLE 1. Rate and activation parameters for the thermal ring-closure reaction of $W(CO)_5bpy$ in toluene[a]

Temperature (°C)	Pressure (MPa)	k_{obs}[b] (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})
25	5	0.080 ± 0.002			−10.9 ± 1.1
	25	0.091 ± 0.003			
	50	0.105 ± 0.003			
	75	0.113 ± 0.002			
	100	0.122 ± 0.004			
15	5	0.034 ± 0.001	58 ± 2	−70 ± 7	
25		0.080 ± 0.002			
30		0.126 ± 0.004			
35		0.172 ± 0.009			

[a] $[W(CO)_6] = 2.5 \times 10^{-3}$ M; $[bpy] = 3.75 \times 10^{-2}$ M. [b] Mean value of at least four kinetic runs.

on the substitution behaviour of short-lived intermediates, i.e. ring-opened species in the present investigation. Further studies on the effect of pressure on other photo-induced thermal ring-closure reactions of metal carbonyl complexes are presently underway. We are convinced that the mechanistic discrimination ability of such $\Delta V^{\ddagger}$ data will assist the assignment of the intimate nature of the substitution process.

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