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# Carbon dioxide activation by $ClRe(CO)_3(4\text{-phenylpyridine})_2$: steady state and flash photolysis study

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## Abstract

Flash and steady state photolysis of fac-$ClRe(CO)_3(4\text{-phpy})_2$ (ph, phenyl; py, pyridine) have been studied in $N_2$ and $CO_2$ deaerated acetonitrile solutions containing triethanolamine (TEOA). Irradiations with photonic energies between 300 and 380 kJ $mol^{-1}$ mostly populate the MLCT excited state which is electron transfer quenched by TEOA. The Re-containing radical $ClRe(CO)_3(4\text{-phpy})_2^{\cdot -}$ generated in this process reacts with $CO_2$ to product CO. Spectroscopic and kinetic information about this reaction is reported.

*Keywords:* Carbon dioxide; Steady state photolysis; Flash photolysis

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## 1. Introduction

Much attention has been paid to carbon dioxide fixation in connection with the greenhouse effect and also as a possible carbon source for organic chemicals. Electrochemical $CO_2$ reduction occurs at considerably negative potentials. Therefore its activation has been conducted by transition metal complexes to decrease the overpotential [1–9]. On the other hand, considering that reduction of $CO_2$ is the basis for solar energy storage in plants, many coordination compounds have been used as sensitizers and/or catalysts for activating $CO_2$ photochemically [10–18]. Some Re-containing complexes employed in that role have been shown to mediate the photochemical reduction of carbon dioxide in the presence of a sacrificial electron donor. Although there are few details available concerning the nature of the interaction between the intermediates photogenerated and the $CO_2$, it seems that very interesting chemistry occurs at the Re centre. In order to gain more understanding of the first photochemical steps and some insight about the mechanism of $CO_2$ reduction, we have undertaken a study of the $ClRe(CO)_3(4\text{-phpy})_2/TEOA/CH_3CN/CO_2$ system (ph, phenyl; py, pyridine; TEOA, triethanolamine). Luminescence quenching, continuous photolysis and flash photolysis data are reported in this paper.

## 2. Experimental details

### 2.1. Materials

The Re(I) complex was available from previous work [19–22]. Its purity was assessed by spectroscopy (UV–visible and IR) [19] and elemental analysis. HPLC quality $CH_3CN$ (Mallinckrodt) was used without further purification and triethanolamine (Carlo Erba) was used as received. Solutions were either purged with nitrogen (Matheson Co.) or saturated with carbon dioxide (commercial grade).

### 2.2. Equipment and procedures

Since the apparatus employed in the flash photolysis experiments has been described previously [23,24], only a few important features will be summarized here. Pulses of polychromatic light with a duration of about 50 μs were obtained from two FP8-100C xenon flashlamps (Xenon Corp.) fired simultaneously at stored electrical energies of 40–250 J $pulse^{-1}$. The wavelength region above 320 nm was isolated by means of a cut-off filter. Photogenerated transients were detected op-

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tically with an analysing light beam directed through the sample cell. The output of the detector phototube, fed into an appropriate sample-hold circuit, was digitized and processed on a personal computer. A fresh solution of photolyte, deaerated with streams of $N_2$ or $CO_2$, was used for each irradiation.

UV-visible spectra were recorded on a Zeiss PMQ 3 spectrophotometer and quenching experiments were carried out in the total fluorescence accessory of a Cary 13 spectrophotometer. Luminescence spectra were taken with an SLM 8000 spectrofluorimeter and IR spectra with a Shimadzu IR-435 spectrophotometer.

Steady state photolysis (350 nm) experiments were carried out in an irradiator with appropriate Rayonet lamps. A $Co(NH_3)_5Br^{2+}$ actinometer was used for the measurement of light intensities [19,25]. In a typical photochemical run, 4 ml of TEOA/$CH_3CN$ solution containing $ClRe(CO)_3(4\text{-phpy})_2$, bubbled for 15–30 min with either $N_2$ or $CO_2$, was placed in a 1 cm rectangular quartz cell. The concentrations of the photolytes were adjusted for absorbing more than 99.99% of the incident light and magnetic bars were used for stirring the solutions while they were irradiated. All experiments were carried out at room temperature.

### 2.3. Product analysis

A known volume of gas from the headspace above the photolysed solution was removed with a syringe (inserted into the cell through a rubber septum) and analysed for CO and $H_2$ by gas chromatography. The equipment and procedures employed in this analysis have been described elsewhere [26]. The production of formic acid was checked using the chromotropic acid spot test [9,27].

## 3. Results

An acetonitrile solution of $ClRe(CO)_3(4\text{-phpy})_2$ that has been thoroughly deaerated by bubbling with $N_2$ displays a broad luminescence band with a maximum at $\lambda_{max} = 540$ nm [20].

We monitored the quenching with TEOA and found that it follows typical Stern–Volmer kinetics. As seen in Fig. 1, a plot of $I^\circ/I$ vs. [TEOA] ($I^\circ$ and $I$ are the luminescence intensities in the absence and presence of quencher respectively) is linear with a slope, the Stern–Volmer constant ($K_{sv}$), equal to 29.7 $M^{-1}$. Taking into account the excited state lifetime, the bimolecular rate constant $k_q = 4.0 \times 10^7$ $M^{-1}$ $s^{-1}$ can be obtained. The same kinetics is observed for solutions saturated with $CO_2$ (Fig. 1).

The UV-visible and IR spectra of $ClRe(CO)_2(4\text{-phpy})_2$ in either $N_2$- or $CO_2$-bubbled acetonitrile solutions show no differences.

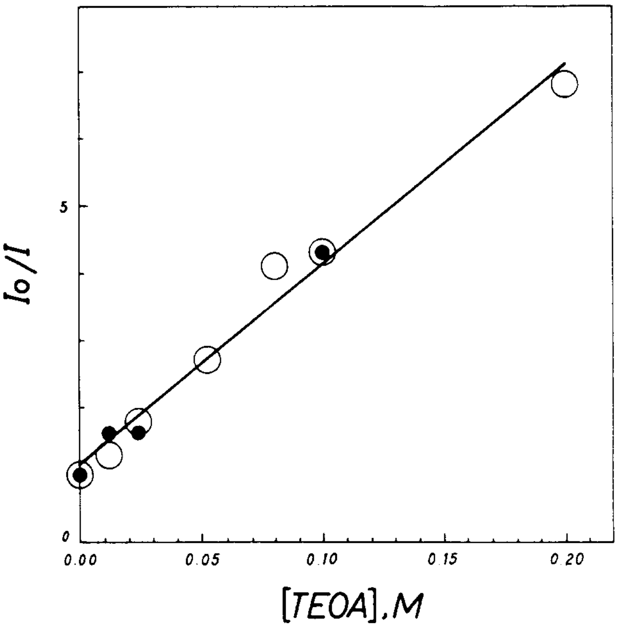


Fig. 1. Stern–Volmer kinetics of the luminescence quenching of fac-$ClRe(CO)_3(4\text{-phpy})_2$ with TEOA in deaerated acetonitrile solutions: ○, $N_2$ bubbled; ●, $CO_2$ bubbled.

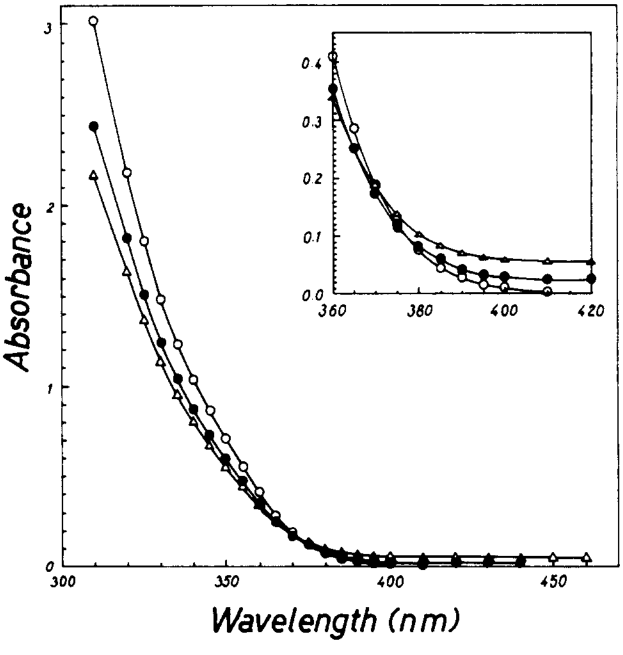


Fig. 2. UV–visible spectral changes following 350 nm steady state photolysis of $6 \times 10^{-4}$ M fac-$ClRe(CO)_3(4\text{-phpy})_2$ in $CO_2$-deaerated acetonitrile solutions containing [TEOA] = 0.75 M for various times (minutes): ○, 0; ●, 10; △, 20 (optical path length 0.2 cm).

$CO_2$-saturated solutions of the rhenium complex undergo important spectral changes upon continuous irradiation. As photolysis proceeds, the intensity of the charge transfer absorption band at 305 nm decreases and a new band is developed between 400 and 450 nm (Fig. 2). The absence of isobestic points is indicative of the formation of at least two absorbing species in relative amounts that vary during the photolysis. These facts complicate the measurement of quantum yield owing to time-dependent changes in absorbance at the irradiating wavelength and possible secondary photolysis effects. To minimize these difficulties, the quantum yield of CO formation, $\phi_{CO}$, was determined at short irradiation times.

As depicted in Fig. 3, a different behaviour is found for the same solutions bubbled with $N_2$ and continuously irradiated under similar photochemical conditions. The MLCT absorption band falls faster and a less significant absorption growth is present at wavelengths longer than 400 nm.

No spectral changes were observed upon keeping the solutions of the complex in TEOA/$CH_3CN$ in the dark.

In a large-scale photolysis experiment, 30 ml of a $1.0\times10^{-1}$ M solution of $ClRe(CO)_3(4\text{-phpy})_2$ and 0.75 M TEOA in $CH_3CN$ was placed in a round bottomed quartz flask, deaerated with $CO_2$ for 20 min and irradiated with 350 nm light from a Rayonet lamp ($I_o\approx6.7\times10^{-6}$ einstein dm$^3$ s$^{-1}$) for 3 h. Analysis of the gas above the solution revealed that CO had been produced. In contrast, no $H_2$ was detected and the presence of formic acid was not evidenced either. If solutions are deaerated with $N_2$, CO is also formed. This is because at low photonic energies such as those used here, some complex decomposition still takes place [19]. However, its quantum yield $\phi^{o}_{CO}$ is significantly lower, the ratio $\phi_{CO}/\phi^{o}_{CO}$ being 3.3. All quantum yields measured are given in Table 1.

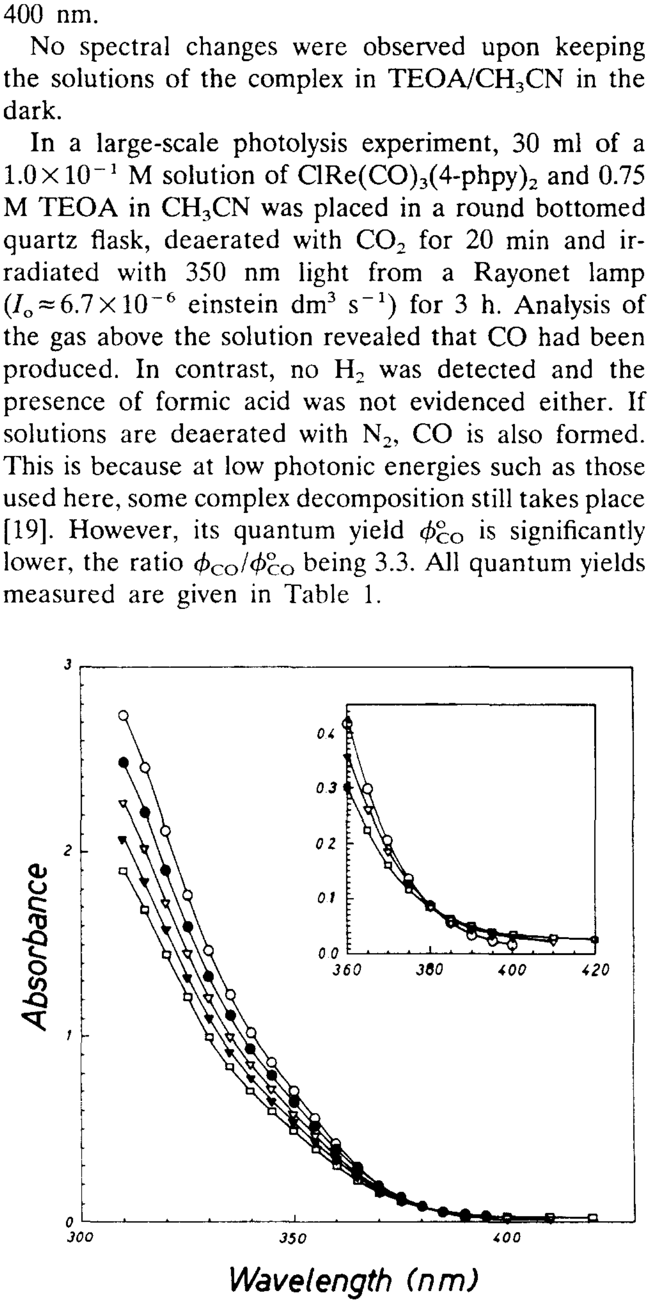


Fig. 3. UV–visible spectral changes following 350 nm steady state photolysis of $6\times10^{-4}$ M fac-$ClRe(CO)_3(4\text{-phpy})_2$ in $N_2$-deaerated acetonitrile solutions containing [TEOA] = 0.75 M for various times (minutes): ○, 0; ●, 2; ▽ 4; ▼ 6; □, 8 (optical path length 0.2 cm).

Table 1
CO quantum yields from steady state irradiations of $ClRe(CO)_3(4\text{-phpy})_2$: (a) nitrogen-bubbled $CH_3CN$ solutions; (b) nitrogen-bubbled 0.75 M TEOA/$CH_3CH$ solutions; (c) $CO_2$-bubbled 0.75 M TEOA/$CH_3CN$ solutions. In each case $I_o\approx6.7\times10^{-6}$ einstein dm$^3$ s$^{-1}$ and the irradiation time was 3 h

| | (a) | (b) | (c) |
|---|---|---|---|
| $\phi_{CO}/10^{-3}$ | 3.8 | 2.2 | 7.3 |

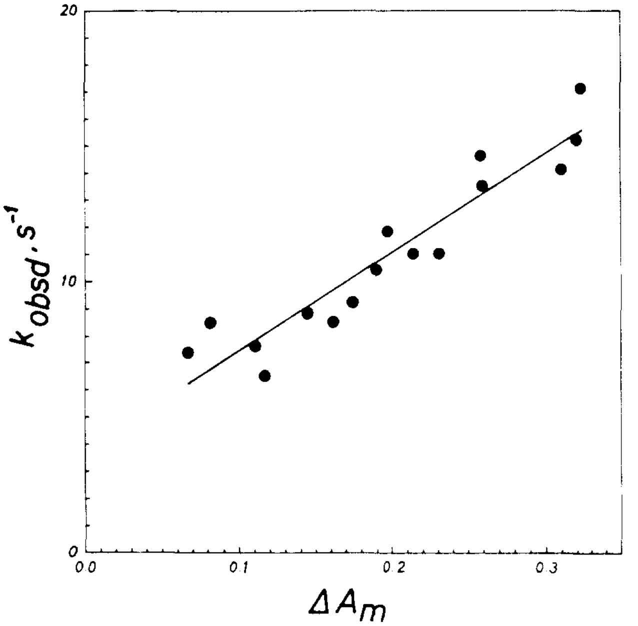


Fig. 4. Dependence of observed rate constant ($k_{obsd}$) on maximum optical density change ($\Delta A_m$) for the exponential decay of the intermediate generated by flash photolysis of $1\times10^{-4}$ M fac-$ClRe(CO)_3(4\text{-phpy})_2$ in $N_2$-bubbled 0.75 M TEOA/$CH_3CN$ solutions (monitoring wavelength 540 nm).

Flash photolysis of $ClRe(CO)_3(4\text{-phpy})_2$ in a nitrogen-bubbled 0.75 M TEOA/$CH_3CN$ solution (all the excited state species formed are quenched at this quencher concentration) induces a fast (within the flash lifetime) increase in absorbance. The differential spectra determined at various times after the flash are identical, suggesting that they arise from a single absorbing species. The decay of the intermediate follows the exponential rate law given by Eq. (1), where $k_{obsd}$, the observed rate constant, adapts to the expression in Eq. (2):

$$\Delta A=\Delta A_m \exp(-k_{obsd}t) \quad (1)$$

$$k_{obsd}=3.8+36.2\Delta A_m \quad (2)$$

This form for $k_{obsd}$, obtained from a curve-fitting analysis of the experimental data points (Fig. 4), is consistent with a competition between first-order and second-order decay paths for the intermediate.

Flash photolysis of the complex in a 0.75 M TEOA/$CH_3CN$ solution saturated with $CO_2$ produces transient absorbance changes that are different from those ob-

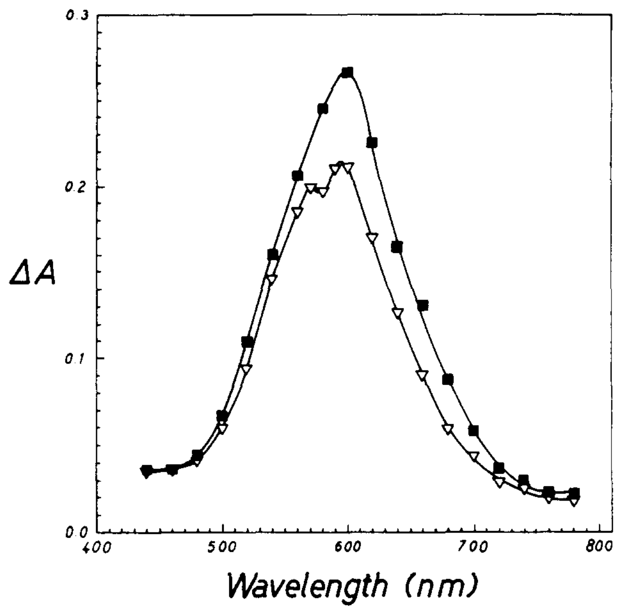


Fig. 5. Transient spectra recorded in flash photolysis irradiations of $1\times10^{-4}$ M fac-ClRe(CO)$_3$(4-phpy)$_2$ in CO$_2$-deaerated 0.75 M TEOA/CH$_3$CN solutions 5 ms after the flash (■) and N$_2$-deaerated 0.75 M TEOA/CH$_3$CN solutions 50 ms after the flash (▽).

Table 2
Observed constants for the exponential decay in transient absorption upon flash photolysis of ClRe(CO)$_3$(4-phpy)$_2$ in CO$_2$/TEOA/CH$_3$CN [a]

| $E$ (J pulse$^{-1}$) [b] | $k_{obsd}\times10^{-2}$ (s$^{-1}$) [c] |
|---|---|
| 32.4 | 1.16 |
| 48.4 | 1.19 |
| 78.4 | 1.16 |
| 84.1 | 1.12 |
| 108.9 | 1.21 |
| 136.9 | 1.18 |

[a] Solutions of $1\times10^{-4}$ M ClRe(CO)$_3$(4-phpy)$_2$ in CO$_2$-deaerated 0.75 M TEOA/CH$_3$CN.

[b] Flash energy in joules per pulse.

[c] Monitoring wavelength for transient absorption decay is 600 nm.

served in the nitrogen-bubbled solution (Fig. 5). In the former, however, the absorbance that grew during the flash lifetime decays faster according to a single exponential with an observed rate constant $k_{obsd}=117$ s$^{-1}$, independently of the flash energy in the range 30–140 J pulse$^{-1}$ (Table 2). The intermediate spectrum does not change either during its decay, thus evidencing also the presence of a single species.

## 4. Discussion

The emission of ClRe(CO)$_3$(4-phpy)$_2$ comes from an Re → 4-phpy charge transfer (CT) excited state; however, its long lifetime (780 ns) can be attributed to some considerable admixture of IL and CT character [19,28]. It has been observed [29] that the reduction potential of this excited state is high enough for it to be susceptible to reductive quenching by TEOA:

$$\mathrm{MLCT(Re \longrightarrow L) + TEOA \longrightarrow [ClRe(CO)_3(phpy)_2]^{\bullet -} + TEOA^{\bullet +}} \quad (3)$$

This process (Eq. (3)) follows the same typical Stern–Volmer kinetics irrespective of whether N$_2$-bubbled solutions or CO$_2$-saturated ones are used, indicating that carbon dioxide does not react with the MLCT state but with some species produced by the quenching step. Moreover, no spectroscopic evidence was found showing that the CO$_2$ binds to the complex before irradiation.

Flash photolysis experiments in N$_2$-purged solutions show that a transient species is produced. In agreement with previous findings [29], we can assess it as the 19-electron Re species [ClRe(CO)$_3$(4-phpy)$_2$]$^{\bullet -}$. Previous laser experiments [25] have shown that no delay occurs between the disappearance of the MLCT excited state and the appearance of the radical. Under the present conditions it decays with mixed second- and first-order kinetics. The formally Re(0) species is labile [30] and substitution by the solvent can occur releasing Cl$^-$, followed by partial dimerization, as has been observed in the electrochemical reduction of fac-Re(dmbipy)(CO)$_3$Cl [31]. In our case the existence of dimerization can be inferred from the absorption growth beyond 380 nm during steady state photolysis, which is typical for Re(I) dimers [19]. However, a second-order reaction such as back electron transfer involving the Re-containing radical and TEOA$^+$ cannot be ruled out, though this reaction would not be of much importance regarding the high reactant consumption observed. The second-order dimerization process detected during the photolysis of ClRe(CO)$_3$(4-phpy)$_2$ in the absence of TEOA has been reported to be slower than the one we observed in our flash photolysis experiments [19]. As a consequence, the more probable events explaining the mixed kinetics observed are

$$\mathrm{ClRe(CO)_3(4\text{-}phpy)_2^{\bullet -} + CH_3CN \longrightarrow (CH_3CN)Re(CO)_3(4\text{-}phpy)_2 + Cl^-} \quad (4)$$

$$\mathrm{ClRe(CO)_3(4\text{-}phpy)_2^{\bullet -} + TEOA^+ \longrightarrow ClRe(CO)_3(4\text{-}phpy)_2 + TEOA} \quad (5)$$

On the other hand, flash photolysis in the presence of CO$_2$ leads to a different transient absorption spectrum which decays through typical first-order kinetics. These results provide direct observation of the reaction between CO$_2$ and the photogenerated Re-containing radical to generate a new transient species during the flash lifetime. Presumably this intermediate is an Re complex with CO$_2$ coordinated which decomposes leading to CO formation and partial regeneration of the parent complex, as indicated by the lower complex consumption during the steady state photolysis of $CO_2$-bubbled solutions. The formation of an intermediate $CO_2$-containing complex is supported by previous evidence of $CO_2$ insertion into rhenium hydride complexes [32,33] and by the attack of $CO_2$ on fac-$Re(dmbipy)(CO)_3Cl^{\cdot-}$ observed in the electrochemical reduction of its parent complex [31].

In a related system [29] a reaction between the ground state of the complex and $TEOA^{\cdot}$ has been reported and as the source of $TEOA^{\cdot}$ the following reaction was proposed: $TEOA^{\cdot+} + TEOA \rightarrow TEOAH^{+} + TEOA^{\cdot}$.

In the present case a carbon monoxide quantum yield value higher than that found [19] for the luminescent excited state generation suggests that such a reaction could also be taking place.

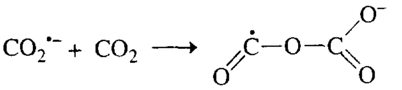
Surprisingly, the CO quantum yield in $N_2$-bubbled solutions containing TEOA is lower than that found in the absence of the sacrificial electron donor. However, considering that the primary processes leading to complex decomposition have been proposed to be [34]

$$ClRe(CO)_3(4\text{-phpy})_2 + h\nu \longrightarrow [ClRe(CO)_3(4\text{-phpy})^{\cdot+}, (4\text{-phpy})^{\cdot-}] \quad (6)$$

$$[ClRe(CO)_3(4\text{-phpy})^{\cdot+}(4\text{-phpy})^{\cdot-}] \longrightarrow ClRe(CO)_3(4\text{-phpy})^{\cdot+} + 4\text{-phpy}^{\cdot-} \quad (7)$$

this result can be rationalized. Since the viscosity of the solution containing TEOA is higher, the recombination of caged geminate products is favoured [35] and so a lower amount of CO must be produced.

Finally, some speculations can be made about the route leading to CO production. For instance, radical species of Re containing $CO_2$ can decompose, regenerating the parent complex and releasing the $CO_2^{\cdot-}$ radical. The latter, in a medium of low proton availability, can evolve through the following sequence [36,37] to produce CO:



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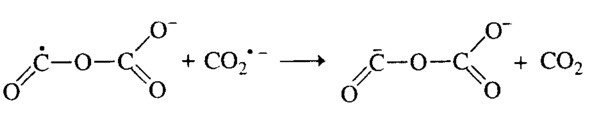

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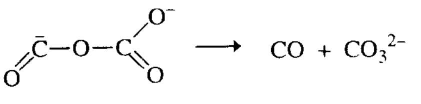


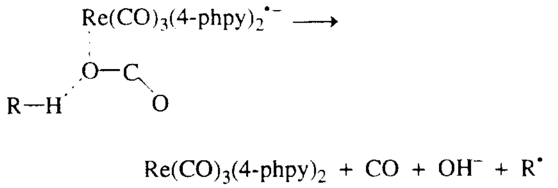
(10)

However, such a mechanism involves the consumption of two $CO_2^{\cdot-}$ radicals by each CO formed. This is not in agreement with our quantum yield results. An alternative path could be

$$ClRe(CO)_3(4\text{-phpy})_2\text{–}CO_2^{\cdot-} + H\text{–}R \longrightarrow ClRe(CO)_3(4\text{-phpy})_2 + CO + OH^- + R^{\cdot} \quad (11)$$

where H–R represents solvent or TEOA.

In reaction (11) an Re(II) intermediate could be involved [38]. Such a step appears to be a counter-thermodynamic one [39]. However, a concerted mechanism can eliminate the need for such an intermediate:



(12)

Since the identity of the $CO_2$-containing intermediate still remains uncertain, more research is needed on its composition, structure and subsequent reactivity.

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