

Preliminary Note

Fluorescence lifetime and quantum yield measurements of the carbonyl(3,5-di-*tert*-butyl-*o*-quinone)rhenium radical in solution

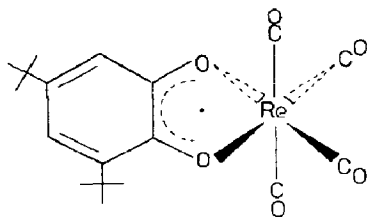
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1. Introduction

In recent years we have extended our studies on quinone photochemistry to include interactions with organometals as well as with carbonyls of metals such as rhenium, manganese, tungsten, chromium and molybdenum. For the series of radical complexes containing rhenium carbonyl, trapping using *o*-quinones has produced some extremely stable species, some of which exhibit optical activity. These radical complexes have been successfully isolated by an integral electron spin resonance-high pressure liquid chromatography (HPLC) technique. The ability to prepare these radical complexes photochemically and to isolate them in pure form by HPLC has opened up many possibilities for detailed spectroscopic studies including emission-fluorescence characterization [1 - 3]. Very few organic radical systems have been quantitatively characterized by fluorescence quantum yield and lifetime measurements at room temperature and in solution. In this note we wish to report the first full optical characterization of the carbonyl(3,5-di-*tert*-butyl-*o*-quinone)rhenium (ReCO_4^- -DTBQ) radical in cyclohexane at room temperature. The structure of this radical is



2. Experimental details

DTBQ (Aldrich) and anthracene were vacuum sublimed before use. $\text{Re}_2(\text{CO})_{10}$ was supplied by Strem Chemicals. Spectroscopic grade cyclohexane was purified by treatment with concentrated sulphuric and nitric acid followed by washing with water and distillation before being stored and dried over sodium. The photochemical reaction of the quinone with rhenium carbonyl has been fully described elsewhere [1, 2] and the resultant stable

$\text{Re}(\text{CO})_4^+ \text{-DTBQ}$ radical was isolated by HPLC as described in our previous papers [1 - 3]. However, some modifications have been incorporated into our HPLC apparatus since the early experiments. Currently we are using a Waters radical compression system with a 5 μm silica-packed cartridge column. The retention time of the $\text{Re}(\text{CO})_4^+ \text{-DTBQ}$ radical was 480 s at a flow rate of 0.5 ml min^{-1} , using cyclohexane as the eluent.

Fluorescence spectra of the pure $\text{Re}(\text{CO})_4^+ \text{-DTBQ}$ radical in cyclohexane were recorded using a Varian SF300 spectrofluorometer at excitation wavelengths between 220 and 280 nm. Fluorescence lifetime measurements were carried out at the Photochemical Research Associates Laboratory (PRA) using a PRA model 3000 single-photon counting instrument. The excitation was at 260 nm while the emission lifetime was monitored at 290 nm.

Fluorescence quantum yields were determined by comparison with a standard anthracene solution [4, 5]. The integrated emission intensity of the radical was compared with that of anthracene. Corrections were made to compensate for any emission due to solvent impurities, Raman and Rayleigh scattering etc. as well as for self-absorption. Obviously, it was also necessary to take into account the difference in absorbance at each excitation wavelength between anthracene and the radical. Since measurements for both the radical and anthracene were made in a cyclohexane solvent, it was not necessary to apply a refractive index correction to our results [4, 6]. All the solutions were thoroughly degassed using nitrogen in order to minimize fluorescence quenching by oxygen [4]. The fluorescence quantum yield of anthracene was taken to be 0.27 ± 0.03 [4, 7 - 11] and was further assumed to be independent of the excitation wavelength in the range used in the experiments [12].

3. Results and discussions

The electronic absorption spectrum of $\text{Re}(\text{CO})_4^+ \text{-DTBQ}$ in cyclohexane is shown in Fig. 1. The spectrum exhibits an intense UV band ($\lambda_{\text{max}} = 230$ nm) and a weak visible band ($\lambda_{\text{max}} = 500$ nm). These results were in agreement with those observed in benzene solution [1]. Also shown in Fig. 1 is the corrected and normalized fluorescence spectrum of the radical in cyclohexane ($\lambda_{\text{ex}} = 230$ nm). The wavelength of maximum emission was at 320 nm. This maximum was constant throughout the excitation wavelengths between 230 and 250 nm, indicating that only one fluorescent species absorbs radiation in this region. The maximum integrated fluorescence band intensity was observed for $\lambda_{\text{ex}} = 230$ nm which corresponds to the absorption maximum of the radical. No fluorescence was observed when the radical was excited at wavelengths corresponding to the visible band. The lack of fluorescence in the visible band may suggest that the corresponding state would be a quartet instead of a doublet. Although doublet-quartet transitions would be spin forbidden, the presence and dominance of the rhenium atom in the radical may lead to a substantial spin-orbit interaction, thus allowing for a weak transition [13].

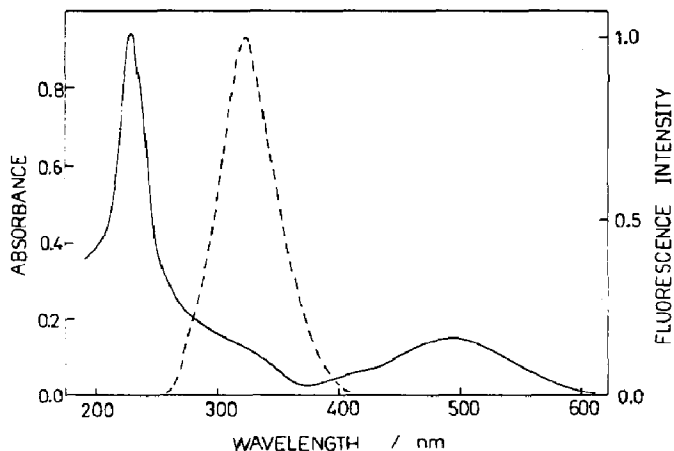


Fig. 1. The absorption (—) and “normalized” fluorescence emission (---) spectra of $\text{Re}(\text{CO})_4^+-\text{DTBQ}$ at room temperature in cyclohexane.

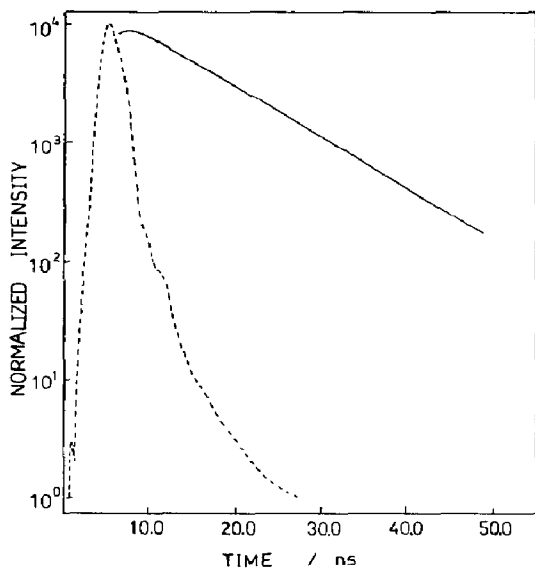


Fig. 2. The fluorescence decay of the $\text{Re}(\text{CO})_4^+-\text{DTBQ}$ radical at room temperature in cyclohexane: ---, excitation pulse; —, calculated decay.

The fluorescence quantum yield of the $\text{Re}(\text{CO})_4^+-\text{DTBQ}$ radical was measured to be 0.06 ± 0.01 compared with anthracene as the standard. This value was independent of the excitation wavelengths between 230 and 250 nm. The small quantum yield of fluorescence of this radical is not too surprising, since the parent quinone did not exhibit fluorescence emission at all at room temperature [14].

A typical fluorescence decay curve for the $\text{Re}(\text{CO})_4^+-\text{DTBQ}$ radical at room temperature in cyclohexane is shown in Fig. 2. The fluorescence lifetime of the radical was found to be 10.3 ± 0.1 ns. The measurement was carried out at an excitation wavelength of 260 nm. Owing to the grating

limitation of the instrument, it was not possible to lower the excitation wavelength beyond 260 nm as we had done in the quantum yield measurements. However, this lifetime value for such a bulky radical is certainly reasonable and the measurement represents one of the very few published data available for radical fluorescence lifetimes at room temperature. Further experiments with optically active radicals in optically active solvents in which circular dichroic light will be used for excitation are planned for the near future.

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