Photofragmentation Kinetics of Some Triruthenium Carbonyl Clusters†

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The photokinetics of fragmentation reactions of [$Ru_3(CO)_{12}$] with L = PPh_3, $P(OPh)_3$, $AsPh_3$, CO, 1-octene, and methyl acrylate in a variety of solvents have been studied. Quantum yields increase to limiting values at high [L] but the limiting values vary significantly with the nature of L. The low efficiency of photochlorination in chlorocarbon solvents, the absence of inhibition by CO of reactions with L = PPh_3, and the absence of appropriate effects of varying incident light intensity all suggest that the first kinetically significant product is a non-radical reactive isomer of [$Ru_3(CO)_{12}$]. This can revert to [$Ru_3(CO)_{12}$] or react with L to form [$Ru_3(CO)_{12}L$] which itself can revert to [$Ru_3(CO)_{12}$] or undergo fragmentation. The former choice governs the rate of increase with [L] to a limiting quantum yield whereas the latter choice governs the dependence of the values of the limiting quantum yield on the nature of L. This scheme is also applicable to photoreactions of [$Os_3(CO)_{12}$] and the quantitative behaviour of the two clusters is not significantly different. Only lower limits for quantum yields for formation of the reactive isomers can be deduced from the data and it remains possible that the primary photophysical process is the formation of a very short-lived diradical by homolysis of a metal–metal bond. Photokinetic studies of reactions of [$Ru_3(CO)_9L_3$] with L (L = PPh_3 or PBu^n_3) are also reported.

Photolysis of metal carbonyl clusters produces intermediates that can act as catalysts for hydrogenation, isomerization, hydrosilation, and polymerization of alkenes.[1,2] Johnson *et al.*[3] were the first to demonstrate the synthetic efficiency of photolysis of [$Ru_3(CO)_{12}$] in forming mononuclear complexes in quantitative yields. Photolysis does not necessarily lead to fragmentation, photosubstitution into the intact cluster also being common,[1,2] and photo-oxidation is also known.[4] In spite of these extensive studies little clear evidence for the nature of the primary photoproducts has emerged and very few detailed kinetic studies have been reported.

Initial reports[5,6] on some photokinetics of [$Ru_3(CO)_{12}$] with longer-wavelength irradiation suggested that photofragmentation, or even photohomolysis of one Ru–Ru bond, was not occurring and that the initial thermally equilibrated product was a chemically reactive isomer of [$Ru_3(CO)_{12}$]. Later papers reported flash photolysis studies of the isomer[2] and also showed that photodissociation of CO became increasingly important as more energetic light was used.[2,7] Photoisomerization was also shown to be important in the longer-wavelength photolysis of [$Os_3(CO)_{12}$][8] and very similar reaction schemes were proposed for both [$Ru_3(CO)_{12}$][2,5] and [$Os_3(CO)_{12}$][8] even though photolysis of the latter often leads to substitution rather than fragmentation.[8,9]

One singular result of the studies of [$Os_3(CO)_{12}$] was the small but significant difference in the limiting quantum yields observed at high concentrations of $P(OEt)_3$ and 1-octene, a feature that had been suggested by the earlier studies of [$Ru_3(CO)_{12}$].[5] We have extended our investigations of this aspect of the photolysis by detailed and precise measurements of the increase of quantum yields for reactions of [$Ru_3(CO)_{12}$] with increasing concentrations of a number of reactants. The results show that the limiting quantum yields vary significantly with the nature of the reactants. Some data for photolysis of [$Ru_3(CO)_9(PPh_3)_3$] with PPh_3 and [$Ru_3(CO)_9(PBu^n_3)_3$] with PBu^n_3 are also reported.

Experimental

The cluster [$Ru_3(CO)_{12}$] (Strem Chemicals) was used as received. Solvents were distilled and stored over molecular sieves, and solutions were deoxygenated when required by bubbling with argon for 10—15 min before photolysis. Reacting ligands were either purified by standard procedures or used as received. The course of the reactions was generally monitored by i.r. spectroscopy of samples taken at regular intervals from degassed solutions contained in Schlenk tubes at an ambient temperature of 22 ± 1 °C. For quantitative photokinetics, reacting solutions ([complex] = *ca.* 10^{-5}—10^{-4} mol dm^{-3}) were contained in tightly stoppered silica cuvettes (path length 10 mm) that were completely enveloped by the light beam from a water-cooled Hanovia high-pressure quartz mercury vapour lamp.[5,8] Suitable Corning filters were used to transmit only the required wavelength of light, λ(irr.). Light intensities were measured by Aberchrome 540[8,10] (φ at 436 nm = 0.06) or ferrioxalate actinometry. Competitive thermal reactions were shown to be unimportant. The well known complexes [$Ru_3(CO)_9(PPh_3)_3$] and [$Ru_3(CO)_9(PBu^n_3)_3$] were synthesized by published methods[11] and their purity confirmed spectroscopically.

Results

The Course of the Reactions.—Photolysis of [$Ru_3(CO)_{12}$] at λ(irr.) = 436 nm with PPh_3 in cyclohexane led quantitatively to a mixture of [$Ru(CO)_4(PPh_3)$], as the major product, together with small amounts of [$Ru(CO)_3(PPh_3)_2$]. The molar absorption coefficients of the bands at 2 036 cm^{-1} (ε 15 000 dm^3 mol^{-1} cm^{-1}) due to [$Ru(CO)_4(PPh_3)$] and at 1 956 cm^{-1} (ε 8 000 dm^3 mol^{-1} cm^{-1}) due to [$Ru(CO)_3(PPh_3)_2$] enabled the yield of the latter to be estimated as $\lesssim 10\%$ and this remained constant throughout the reactions. Photolysis at 366 nm, on the other hand, led to [$Ru(CO)_4(PPh_3)$] and larger amounts of [$Ru(CO)_3(PPh_3)_2$], the relative yield of which increased steadily throughout the reactions. In addition, appreciable yields of [$Ru_3(CO)_9(PPh_3)_3$] were indicated[2,7] by the

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† *Non-S.I. units employed:* atm = 101 325 Pa.

appearance of a band at 500 nm. Because of the complications introduced by photodissociation of CO at higher light energies[2,7] the photokinetics with ligands other than CO were studied only with 436-nm light.

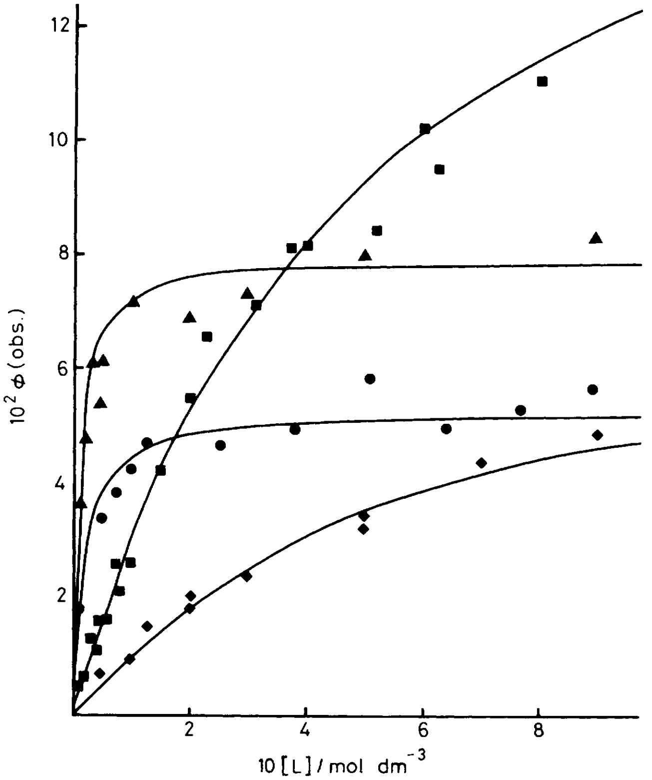


Figure. Dependence of φ(obs.) on [L]: (▲) L = 1-octene in iso-octane; (●) L = $P(OPh)_3$ in cyclohexane; (■) L = PPh_3 in benzene; (◆) L = 1-octene in benzene. All the lines drawn are based on the parameters *a*φ(lim.) and *a*, derived as described in the text

Photolysis of $[Ru_3(CO)_{12}]$ at 436 nm with $P(OPh)_3$ in cyclohexane led to complete loss of $[Ru_3(CO)_{12}]$ and appearance of i.r. bands at 2 076m, 2 016s, 2 004s, 1 980s, and 1 970s cm^{-1} that correspond closely to bands shown by $[Ru(CO)_4\{P(OPh)_3\}]$ formed by the rapid reaction of $[Ru(CO)_4(C_2H_4)]$[3] with $P(OPh)_3$. A quite intense band at 1 940 cm^{-1}, assignable to $[Ru(CO)_3\{P(OPh)_3\}_2]$, was also observed but its formation was not studied quantitatively.

Photolysis with $AsPh_3$ was accompanied by growth of a band at 1 960 cm^{-1}, assignable to $[Ru(CO)_3(AsPh_3)_2]$, together with bands at 1 990, 2 000, and 2 080 cm^{-1}. These are in good agreement with those reported for $[Ru(CO)_4(AsPh_3)]$,[12] the band at 2 060 cm^{-1} due to the latter being obscured by unreacted $[Ru_3(CO)_{12}]$ since this reaction was not monitored to completion.

Photolysis with 1-octene led to growth of bands at 2 110m, 2 020s, and 1 996m,br cm^{-1} in good agreement with those obtained[13] with 1-pentene and characteristic of $[Ru(CO)_4(1\text{-alkene})]$.[13] Photolysis with ethyl acrylate was only carried out in benzene, and i.r. data were not obtained. However, $[Ru(CO)_4(CH_2{=}CHCO_2Me)]$ is a known product of photolysis of $[Ru_3(CO)_{12}]$ with methyl acrylate.[14] Reactions with CO at 313, 366, and 436 nm in cyclohexane or iso-octane all went quantitatively to form $[Ru(CO)_5]$ as reported elsewhere,[3,5–7] as did reactions of $[Ru_3(CO)_9L_3]$ with L to form $[Ru(CO)_3L_2]$ (L = PPh_3 or $PBu^n{}_3$).

Photokinetics of the Reactions.—All the reactions were accompanied by the disappearance of the absorbance band at 390 nm due to $[Ru_3(CO)_{12}]$. The final absorbance at 390 nm was usually 5—10% of the initial absorbance, and never more than *ca.* 15%. Absorbance changes at 390 and 436 nm were generally followed over the first 30—50% completion of reaction. Rates were then calculated[8] from 4—6 pairs of absorbances measured during a particular run and by making use of the value $\varepsilon = 7.3 \times 10^4$ dm^3 mol^{-1} cm^{-1} for $[Ru_3(CO)_{12}]$ at 390 nm in hydrocarbon solutions. The individual rates were then averaged. Alternatively, what must have been accidentally linear plots of $\ln(A_t - A_\infty)$ *vs.* time were

Table 1. Quantum yields for reactions of $[Ru_3(CO)_{12}]$ with PPh_3 in benzene; λ(irr.) = 436 nm

	10^2φ(obs.) at $10^5[Ru_3(CO)_{12}]$/mol dm^{-3} =						
$[PPh_3]$/mol dm^{-3}	1.25	2.5	6.25	11.9[a]	12.5	24.0	σ[φ(obs.)][b]/%
0.010					0.54		
0.020	0.54	0.51	0.51	(0.20)[c]	0.84	0.69	23
0.030					1.33		
0.040	0.97	0.94	1.04	1.34	1.58	1.39	22
0.050					1.68		
0.060	1.39	1.14	1.45	1.83	2.30	1.94	26
0.075					2.65		
0.080	1.63	1.74	2.09	2.09	2.82	2.54	21
0.100	2.14	2.02	3.09	2.47	3.34	3.01	20
0.155					4.29		
0.200	5.46	5.06	5.77	5.61	5.87	5.26	6
0.226					6.60		
0.314					7.15		
0.376					8.18		
0.401	8.64	8.65	9.09	7.64	8.05	6.57	11
0.524					8.45		
0.601	11.8	10.9	10.1	9.19	9.43	9.42	10
0.628					9.53		
0.802	13.9	12.5	10.5	9.86	8.94	10.7	17

[a] Under 1 atm CO. [b] Probable error of an individual measurement of φ(obs.) at a given value of $[PPh_3]$. The method of pooled variances gives a value of ±19% for σ[φ(obs.)] applicable to all values of $[PPh_3]$, and a corresponding value of ±7.8% for the average, φ(av.), of six values of φ(obs.). [c] Not used in computations.

Table 2. Quantum yields for reactions of $[Ru_3(CO)_{12}]$; λ(irr.) = 436 nm

$[L]/mol\ dm^{-3}$	$10^2\varphi(obs.)$	$[L]/mol\ dm^{-3}$	$10^2\varphi(obs.)$	$[L]/mol\ dm^{-3}$	$10^2\varphi(obs.)$
PPh_3 in cyclohexane		$P(OPh)_3$ in cyclohexane		$P(OPh)_3$ in benzene	
0.01	2.55	0.0026	0.74	0.032	1.55
0.02	3.82	0.0051	1.12	0.064	1.04
0.03	5.46	0.0076	1.60	0.102	1.59
0.04	6.37	0.0102	1.89	0.127	1.71
0.05	6.70	0.0225	2.99	0.254	3.14
		0.0509	3.42	0.508	4.07
PPh_3 in decalin		0.0764	3.89	0.762	4.30
0.02	0.20	0.102	4.27	1.02	5.44
0.29	3.28	0.127	4.73	1.28	6.31
0.38	4.38	0.255	4.67	1.40	5.68
0.51	5.88	0.382	4.97	1.54	5.87
		0.509	5.88	1.78	6.28
$AsPh_3$ in benzene		0.637	4.97	1.92	5.93
0.01	0.28	0.767	5.30	2.16	7.30
0.02	0.62	0.891	5.68	2.30	6.10
0.04	1.04	1.02	5.32	2.55	8.64
0.08	1.94				
0.10	2.32	1-Octene in iso-octane		1-Octene in benzene	
0.15	3.06	0.0051	2.96	0.050	0.71
0.20	3.60	0.0102	3.66	0.100	0.95
0.30	5.68	0.0204	4.82	0.130	1.53[a]
0.40	6.52	0.0306	6.10	0.200	1.87
0.50	7.76	0.0409	5.40	0.200	2.00[b,c]
0.60	7.82	0.0500	6.14	0.300	2.43
0.70	8.21	0.100	7.20	0.500	3.22
		0.200	6.93	0.500	3.48
Ethyl acrylate in benzene		0.300	7.30	0.700	4.40
0.100	1.35	0.500	8.00	0.900	4.88
0.200	2.16	0.900	8.30	1.28	5.33
0.300	2.79	1.28	8.9	1.28	5.21
0.300	2.70	1.28	8.6		
0.300	2.43				
0.300	2.79				

[a] Incident light intensity, $I_0 = 7 \times 10^{-10}$ Einstein cm^{-2} s^{-1}. [b] $I_0 = 17 \times 10^{-10}$ Einstein cm^{-2} s^{-1}. [c] Reaction under 1 atm CO.

Table 3. Reactions of $[Ru_3(CO)_{12}]$ with CO in iso-octane

	$10^2\varphi(obs.)$ at λ(irr.)/nm =		
$10^3[CO]/mol\ dm^{-3}$	313	366	436
0.59	0.36	0.39	0.41
1.76	0.87	0.68 *	0.77
2.92	1.32	1.36	1.37
4.66	1.93	2.45, 2.12	1.89
11.5	3.90	4.40	3.50

* Omitted from least-squares analysis.

obtained and the slopes were multiplied by the initial concentrations of $[Ru_3(CO)_{12}]$ to obtain the rates of reaction at zero time. The intensity of absorbed light was estimated from the transmittance at 436 nm (where the products had negligible absorbance) combined with the intensity of the incident light as obtained from the actinometry. This was usually in the range (7—50) × 10^{-10} Einstein cm^{-2} s^{-1}. The probable error of an individual measurement of φ(obs.) from a single pair of absorbance measurements was generally found to be *ca.* ±20%, the corresponding uncertainty of averages of several values being $\lesssim 10\%$.

The values of φ(obs.) increased with [L] towards a limiting value, φ(lim.), as shown in the Figure, and the data were all in good accord with equation (1) where *a* is a constant. No evidence for decomposition was observed in any of the reactions and values of φ(obs.) were unaffected when a selection of reactant solutions were deoxygenated by bubbling with argon.

$$\varphi(\text{obs.}) = \varphi(\text{lim.})a[L]/(1 + a[L]) \qquad (1)$$

A collection of data for reactions with PPh_3 in benzene is given in Table 1. Reactions were carried out with initial concentrations of $[Ru_3(CO)_{12}]$ varying from 1.25×10^{-5} to 2.4×10^{-4} mol dm^{-3} for several values of $[PPh_3]$. This resulted in values of I_a/I_0 (the ratio of absorbed to incident light intensity) that varied from 0.09 to 0.85. The values of φ(obs.) in Table 1 show no systematic trends with varying I_a/I_0. One set of runs was carried out with solutions equilibrated with CO. Data for reactions with PPh_3 in solvents other than benzene, and for reactions with several other ligands, are given in Tables 2 and 3. Reactions with 1-octene showed a clean isosbestic point at 476 nm up to *ca.* 70% completion of reaction after which it gradually disappeared. Values of A_∞ were estimated by extrapolation of absorbance data for spectra passing through the isosbestic point. Reactions with φ(obs.) < 0.5φ(lim.) showed no effect due to the presence of CO or due to an increase in incident light intensity by a factor of over 2.

Values of φ(lim.) and *a* were found from a linear least-squares analysis of the dependence of 1/φ(obs.) on 1/[L] in which it was assumed that each value of φ(obs.) had the same percentage uncertainty. The inverse of the intercepts gave the value of φ(lim.) and the ratio intercept/gradient gave the values of *a*. Values of σ[φ(obs.)], the probable error of the determination of φ(obs.), were also obtained. These parameters are given in

Table 4. Kinetic parameters for photolysis of $[Ru_3(CO)_{12}]$ with L^a

L	Solvent	N^b	φ(lim.)	$a\varphi$(lim.)/dm^3 mol^{-1}	a/dm^3 mol^{-1}	$\sigma(\varphi)^c$/%
PPh_3	Benzene	75^d	0.186 ± 0.015	0.367 ± 0.013	1.97 ± 0.17	22
PPh_3	Benzene	8^e	0.167 ± 0.021	0.342 ± 0.022	2.04 ± 0.29	10.2
PPh_3	Cyclohexane	5	0.122 ± 0.014	3.12 ± 0.25	25.5 ± 3.6	5.6
PPh_3	Decalin	4	(0.12)	1.14 ± 0.21	*ca.* 10	10.2
$P(OPh)_3$	Benzene	16	0.081 ± 0.004	0.182 ± 0.011	2.25 ± 0.17	9.5
$P(OPh)_3$	Cyclohexane	16	0.053 ± 0.001	2.976 ± 0.144	56.0 ± 3.0	7.5
$P(OMe)_3$	Cyclohexane	5^f	0.044 ± 0.004	3.19 ± 0.21	68 ± 8	8.3
$AsPh_3$	Benzene	11	0.147 ± 0.014	0.286 ± 0.011	1.94 ± 0.19	7.4
1-Octene	Benzene	12	0.074 ± 0.006	0.136 ± 0.008	1.83 ± 0.17	9.6
1-Octene	Iso-octane	13	0.080 ± 0.003	7.67 ± 0.78	96.1 ± 10.3	9.6
Ethyl acrylate	Benzene	6	0.053 ± 0.007	1.81 ± 0.020	3.41 ± 0.059	5.9
CO	Iso-octane	15^g	0.082 ± 0.014	6.18 ± 0.35	75.3 ± 13.2	12.6
CO	Cyclohexane	6^h	0.053 ± 0.011	5.64 ± 0.39	107 ± 23	9.9
CO	Decalin	1	(0.07)	*ca.* 1.5	*ca.* 20	
CO	Benzene	4	(0.07)	*ca.* 0.2	*ca.* 3	
PPh_3^{i}	Benzene	10	0.0105 ± 0.0003	1.11 ± 0.16	106 ± 16	15
$P(OEt)_3$^{j}	Benzene	14	0.0459 ± 0.0024	0.110 ± 0.006	2.4 ± 0.14	5.2
1-Octene^j	Benzene	16	0.0317 ± 0.0004	0.306 ± 0.012	9.6 ± 0.4	6.5

^{a} Analyzed by a weighted least-squares procedure according to equation (1); λ(irr.) = 436 nm except where indicated otherwise. ^{b} The number of individual values of φ(obs.) included in the analysis. ^{c} The probable error of an individual determination of φ(obs.). ^{d} Values taken from Table 1 together with another set not reported here. ^{e} Data for reactions under 1 atm CO (Table 1) analyzed separately. ^{f} Data from ref. 2. ^{g} Analysis of combined data for reactions with λ(irr.) = 313, 366, and 436 nm. ^{h} Analysis of data taken from ref. 5. ^{i} Reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with λ(irr.) = 313 nm. ^{j} Reactions of $[Os_3(CO)_{12}]$; data taken from ref. 8.

Table 5. Quantum yields for reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with PPh_3 in benzene; λ(irr.) = 313 nm

$[PPh_3]$/mol dm^{-3}	$10^3\varphi$(obs.)	$[PPh_3]$/mol dm^{-3}	$10^3\varphi$(obs.)
0.003	2.65	0.10	7.50
0.005	3.25	0.40	11.5
0.010	5.10	0.50	10.8
0.020	7.80	0.65	8.40
0.040	5.10*	0.75	8.75
0.07	11.1		

* Not used in computations.

Table 6. Quantum yields for reactions of $[Ru_3(CO)_9(PBu^n{}_3)]$ with $PBu^n{}_3$ in benzene; λ(irr.) = 366 nm

$[PBu^n{}_3]$/mol dm^{-3}	$10^2\varphi$(obs.)	$[PBu^n{}_3]$/mol dm^{-3}	$10^2\varphi$(obs.)
0.0010	1.29	0.25	0.77
0.0029	1.17	0.35	0.93
0.0039	1.28	0.49	0.87
0.0049	1.09	0.69	0.97
0.016	0.95	0.73	0.94
0.025	0.96	0.82	0.89
0.082	1.05		

Table 4. In the case of photolysis with PPh_3 in decalin, and CO in decalin or in benzene, the limiting quantum yields were not approached closely enough for them to be determined and values of a were estimated approximately by dividing the initial gradient of the dependence of φ(obs.) *vs.* [L] by the limiting quantum yields in solvents where φ(lim.) was approached more closely. Data for photolysis with CO in iso-octane at 313, 366, and 436 nm were previously analyzed[5] for each wavelength separately but quantum yields were not found to depend significantly on wavelength. The parameters in Table 4 have been obtained by pooling 15 values of φ(obs.) obtained at the three wavelengths.

Photofragmentation of $[Ru_3(CO)_9(PPh_3)_3]$ in benzene in the presence of PPh_3 was monitored by measuring the decreasing intensity of its band at 510 nm (ε 7.6 × 10^3 dm^3 mol^{-1} cm^{-1}). Photolysis at 436 nm was very slow, values of φ(obs.) in benzene being constant at *ca.* 7 × 10^{-4} when $[PPh_3] \gtrsim 0.1$ mol dm^{-3}. Photolysis at 313 nm was more efficient and φ(obs.) varied with $[PPh_3]$ (Table 5) in accordance with equation (1), values obtained for φ(lim.) and a being given in Table 4. When unfiltered light was used the limiting rates of reaction with PPh_3 were about the same as those for reactions under 100 or 40% CO.

Photofragmentation of $[Ru_3(CO)_9(PBu^n{}_3)_3]$ with $PBu^n{}_3$ was monitored by measuring the decreasing intensity of its band at 465 nm (ε 10 × 10^3 dm^3 mol^{-1} cm^{-1}). Quantum yields (Table 6) were measured only with λ(irr.) = 366 nm and show a very different dependence on $[PBu^n{}_3]$ from that shown in equation (1). Values of φ(obs.) are constant at (9.3 ± 0.3) × 10^{-3} when $[PBu^n{}_3]$ = 0.02 – 0.80 mol dm^{-3}. However, when $[PBu^n{}_3]$ is decreased the values of φ(obs.) increase to *ca.* 1.3 × 10^{-2} at $[PBu^n{}_3]$ = 0.001 mol dm^{-3}. Very little reaction occurs under 100% CO over 2 h, a time period over which *ca.* 40% reaction with $PBu^n{}_3$ occurs.

Discussion

The values of φ(obs.) for reactions of $[Ru_3(CO)_{12}]$, and of the parameters derived from them according to equation (1), are of good precision. The accuracy of the values of φ(lim).) depends on the accuracy of the actinometry but, since photolysis of $[Ru_3(CO)_{12}]$ with all the reactants other than CO was referenced to the Aberchrome actinometer under identical conditions, the relative values obtained for φ(lim.) are of good accuracy. The photolysis with CO was referenced to ferrioxalate actinometry but this should not affect the relative accuracy of the value of φ(lim.) significantly.[8] The values of a depend only on the rate of rise of φ(obs.) to φ(lim.) and are quite independent of the actinometry. Their precision and accuracy depend, therefore, only on the internal consistency of the data for each reactant and the extent to which larger concentrations of reactant might have environmental effects. The good fit of the data to equation (1), even when [L] is high, suggests that the latter are negligible.

The fragmentation reactions of $[Ru_3(CO)_{12}]$ show exactly the same kinetic behaviour as the photoreactions of $[Os_3(CO)_{12}]$ with $P(OEt)_3$ and 1-octene,[8] and the less extensively studied

$$[M_3(CO)_{12}] \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} [M_3(CO)_{12}]^* \qquad (2)$$

$$[M_3(CO)_{12}]^* \xrightarrow{k_f} [M_3(CO)_{12}]^{**} \qquad (3)$$

$$[M_3(CO)_{12}]^{**} \xrightarrow{k_1} [M_3(CO)_{12}] \qquad (4)$$

$$[M_3(CO)_{12}]^{**} + L \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [M_3(CO)_{12}L] \qquad (5)$$

$$[M_3(CO)_{12}L] \xrightarrow{k_4} [M(CO)_4L + [M_2(CO)_8] \qquad (6)$$

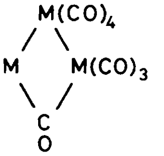
$$[M_3(CO)_{12}L] \xrightarrow{k_5} [M_3(CO)_{11}L]^{**} + CO \qquad (7)$$

$$[M_3(CO)_{12}L] \xrightarrow{k_6} [M_3(CO)_{12}] + L \qquad (8)$$

$$[M_3(CO)_{12}]^{**} + L' \underset{k_3'}{\overset{k_2'}{\rightleftharpoons}} [M_3(CO)_{12}L'] \qquad (9)$$

$$[M_3(CO)_{12}L'] \xrightarrow{k_6'} [M_3(CO)_{12}] + L' \qquad (10)$$

Scheme.



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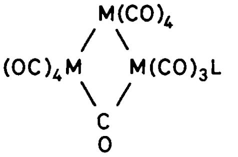

(II)

reactions of $[Ru_3(CO)_{12}]$ with $P(OMe)_3$ and PPh_3.[2,*] Reactions of $[Ru_3(CO)_{12}]$ with PPh_3 and 1-octene in benzene are not detectably affected by the presence of CO which itself has a very low quantum yield for reaction in benzene.[5] This confirms that photodissociation of CO from $[Ru_3(CO)_{12}]$ is insignificant as a primary process at 436 nm as it is for $[Os_3(CO)_{12}]$.[8] Further, the quantum yields for reaction with PPh_3 or 1-octene show no dependence on I_a, even when they are well below the limiting values. This was previously shown to be the case also for reaction of $[Ru_3(CO)_{12}]$ with CO,[5] and of $[Os_3(CO)_{12}]$ with 1-octene,[8] and serves to confirm the conclusion that photofragmentation is not a primary process in any of the long-wavelength photoreactions of these clusters. In addition to the behaviour outlined above, both $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ show Stern–Volmer 'quenching' when Lewis bases are added that do not undergo any photoreaction.[6,8]

The virtual identity of the photokinetic behaviour of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ leads to the Scheme (shown above) appropriate to them both. This scheme is a synthesis of Schemes I and II suggested for $[Os_3(CO)_{12}]$[8] and is expressed here, for consistency, in essentially the same form as the scheme for $[Ru_3(CO)_{12}]$ proposed by Ford and co-workers.[2] The species $[M_3(CO)_{12}]^*$ is the photochemically excited form of $[M_3(CO)_{12}]$. It relaxes to the chemically reactive cluster $[M_3(CO)_{12}]^{**}$ that is isomeric with $[M_3(CO)_{12}]$ and that can rapidly form adducts with Lewis bases L or L′. The Lewis base L is capable of causing further reaction. This reaction is generally fragmentation [reaction (6)] when M = Ru, but when M = Os fragmentation only seems to occur when L = alkene, substitution *via* reaction (7) occuring when L = P-donor. Both reactions (6) and (7) are followed by rapid processes that lead to the ultimately observed products without contributing to the kinetics.† Lewis base L′ is incapable of causing either fragmentation of $[M_3(CO)_{12}L']$ or displacement of CO from it. All it can do is to induce reversion of $[M_3(CO)_{12}L']$ to $[M_3(CO)_{12}]$ with concerted release of L′. The distinction between L and L′ is, however, not absolute (see below). The species $[Ru_3(CO)_{11}L]^{**}$ is a reactive isomer of $[Ru_3(CO)_{11}L]$ to which it decays rapidly, thus completing the substitution process *via* this mechanism as observed for $[Os_3(CO)_{12}]$.[8]

By assuming, with Ford and co-workers,[2] that $(k_4 + k_6) \gg k_3$ and $k_6' \gg k_3'$, the rate equation corresponding to this Scheme is as shown in equation (11) if fragmentation is the only reaction.

$$\varphi(\text{obs.}) = \varphi(\text{max.}) \cdot \frac{k_2[L]}{k_1 + k_2[L] + k_2'[L']} \cdot \frac{k_4}{k_4 + k_6} \qquad (11)$$

If substitution occurs instead then k_4 should be replaced by k_5 or, if both fragmentation and substitution occur, k_4 should be replaced by $(k_4 + k_5)$. The term φ(max.) is the quantum yield, $k_f/(k_f + k_d)$, for formation of the reactive isomer $[M_3(CO)_{12}]^{**}$ and is the maximum value that would be reached at very high [L] if $k_4 \gg k_6$. The term $\varphi(\text{max.})k_4/(k_4 + k_6)$ is the maximum value, φ(lim.), that is actually reached at high [L]. The ratio k_2/k_1 is equal to a in equation (1). Structures (I) and (II) have been suggested, respectively, as possible formulations for the reactive isomer $[M_3(CO)_{12}]^{**}$ and the adduct $[M_3(CO)_{12}L]$ {or $[M_3(CO)_{12}L']$}.[2,5,6] These are convenient in that (I) contains a vacant co-ordination site that can readily be filled by L to form (II) which contains M only in 18-electron configurations. A diradical form for $[M_3(CO)_{12}]^{**}$ produced by simple photohomolysis of a M–M bond is not likely because of the very low quantum yields observed for photolysis in CCl_4 which should scavenge the radicals and form chlorocarbonyl products.[2,5,6,8] It is not impossible, however, that the diradical is, in fact, the immediate product of the relaxation of $[M_3(CO)_{12}]^*$ but that it forms $[M_3(CO)_{12}]^{**}$ so rapidly that it has no opportunity to be scavenged appreciably even in pure CCl_4.[8] This signifies that, although the photokinetics are generally a reflection of the thermal chemistry of intermediates $[M_3(CO)_{12}]^{**}$, $[M_3(CO)_{12}L]$, and $[M_3(CO)_{12}L']$, the photophysics could indeed be appropriately discussed in terms of simple photohomolysis of an M–M bond.[8] Although (I) and (II) are perfectly satisfactory proposals for the structures of $[M_3(CO)_{12}]^{**}$ and $[M_3(CO)_{12}L]$, several other formulations can satisfy the same criteria.[15]

An important feature of the Scheme is that the values of φ(lim.) should be dependent on the nature of L through differences in the 'partitioning ratio' $k_4/(k_4 + k_6)$ which governs whether $[M_3(CO)_{12}L]$ reacts to form products or reverts to $[M_3(CO)_{12}]$. Small but significant differences in φ(lim.) were observed for reactions of $[Os_3(CO)_{12}]$ with $P(OEt)_3$ and 1-octene[8] but the dependence of φ(lim.) on the nature of the nucleophile L that reacts with $[Ru_3(CO)_{12}]$ is much more pronounced because of the wider range of nucleophiles studied. The data in Table 4 suggest that φ(lim.) varies along the series ethyl acrylate $\lesssim$ $P(OMe)_3$ < 1-octene ~ CO ~ $P(OPh)_3$ < $AsPh_3$ $\lesssim$ PPh_3 irrespective of

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[*] Ford and co-workers[2] have reported values of $10^3\varphi(\text{obs.})$ for reactions with PPh_3. In cyclohexane at 405 nm with $[PPh_3] = 0.001$, 0.01, and 0.10 mol dm^{-3}, $10^3\varphi(\text{obs.}) = 2.8 \pm 0.3$, 16 ± 2, and 36 ± 4, respectively. Our kinetic parameters for λ(irr.) = 436 nm (Table 4) lead to corresponding values of 3.07 ± 0.23, 24.8 ± 1.2, and 86 ± 4, respectively. Our values of φ(obs.) for reactions with 1 atm CO in cyclohexane or iso-octane are 40% larger than those of Ford and co-workers[2] but our values at lower partial pressures of CO are about twice as large as theirs. These systematic differences in the rate of increase of φ(obs.) with [L] should not depend on problems with actinometry and the source of the differences is not obvious. They do not, however, affect conclusions reached in this discussion in any substantial way.

[†] The fact that $[Ru(CO)_3L_2]$ [L = PPh_3, $P(OPh)_3$, or $AsPh_3$] are also direct products of photolysis of $[Ru_3(CO)_{12}]$ presumably results from substitution reactions of L with $[Ru_2(CO)_8]$ before it undergoes further fragmentation.

solvent.* Although the difference in φ(lim.) between neighbours in the series is sometimes small the overall range covered by the series exceeds a factor of 3. In fact, the possible range is evidently much greater than this when results[2] for the so-called quenching reagents L′ are included. Lewis bases previously classified as being L′, such as tetrahydrofuran (thf) or diglyme ($\mathrm{MeOCH_2CH_2OCH_2CH_2OMe}$), produce no reaction and this could be accounted for if they were considered as being 'normal' nucleophiles L but with $k_6 \gg k_4 \sim 0$ so that φ(lim.) is insignificant. However, other Lewis bases such as pyridine, cyclohexene, and propionitrile do cause some photofragmentation of $[\mathrm{Ru_3(CO)_{12}}]$[2] so that they are therefore better considered as being examples of L rather than L′. In these cases $k_6 \gg k_4 > 0$ and φ(lim.) is finite, albeit small. The values of φ(lim.) can therefore vary from zero up to at least the value of 0.2 found here for reaction with $\mathrm{PPh_3}$ in benzene.

The highest value of φ(lim.) obtained here provides a lower limit of 0.2 for φ(max.), the 'photophysical' quantum yield. As discussed for the photokinetics of $[\mathrm{Os_3(CO)_{12}}]$,[8] there is nothing in the data obtained so far for these clusters to suggest that φ(max.) could not be unity, the fact that φ(lim.) is less than φ(max.) arising simply from the existence of reaction (8) which is a thermal reaction of the intermediate $[\mathrm{M_3(CO)_{12}L}]$ and has no implications as to the photophysics of the clusters.[8]

The series quoted above for increases in φ(lim.) corresponds to the series of decreasing values of k_6/k_4. Ford and co-workers[2] have obtained values of $(k_4 + k_6)$ from reactions of $[\mathrm{Ru_3(CO)_{12}L}]$ generated by flash photolysis in cyclohexane. These increase along the series thf < cyclohexene < $\mathrm{PPh_3}$ < $\mathrm{P(OMe)_3} \ll$ CO, $\mathrm{C_2H_4}$, the range from $\mathrm{PPh_3}$ to CO being a factor of over 250. The value of 200 $\mathrm{s^{-1}}$ for L = $\mathrm{PPh_3}$ allows us to estimate $k_4 = 25 - 125\ \mathrm{s^{-1}}$ and $k_6 = 175 - 75\ \mathrm{s^{-1}}$ for φ(max.) values in the range 1—0.2. The value of 900 $\mathrm{s^{-1}}$ for L = $\mathrm{P(OMe)_3}$ leads to corresponding values $k_4 = 40 - 200\ \mathrm{s^{-1}}$ and $k_6 = 860$—$700\ \mathrm{s^{-1}}$. The value of k_4 is $\gtrsim 10^2$ times larger for CO than for $\mathrm{PPh_3}$ but the value of k_6 increases even more than this. The greater reactivity of the proposed intermediate $[\mathrm{Ru_3(CO)_{13}}]$ compared with $[\mathrm{Ru_3(CO)_{12}(PPh_3)}]$ might be associated with the much lower nucleophilicity expected for CO towards $[\mathrm{Ru_3(CO)_{12}}]$ since the reversion of $[\mathrm{Ru_3(CO)_{12}L}]$ to $[\mathrm{Ru_3(CO)_{12}}]$ and free L is likely to be related to the reverse of nucleophilic attack on $[\mathrm{Ru_3(CO)_{12}}]$ by L. Data for a wider range of reactants will be required before an answer can be obtained to the question of what factors control the ratio k_6/k_4 although π-acid character and/or small size seem to favour larger values.

Values of k_2/k_1 are given by the values of *a* in Table 4. Those for reactions in benzene are small and hardly affected by the nature of the nucleophile. The values for reactions in saturated hydrocarbons are considerably greater and increase along the series $\mathrm{PPh_3} < \mathrm{P(OPh)_3} < \mathrm{P(OMe)_3}$ < CO < 1-octene. We suggest that this difference in the solvent effect is due to the co-ordinating power of benzene, the result of which is that $[\mathrm{Ru_3(CO)_{12}}]^{**}$ in benzene is solvated, *i.e.* it is $[\mathrm{Ru_3(CO)_{12}(C_6H_6)}]$ which reacts with the ligands L to form $[\mathrm{Ru_3(CO)_{12}L}]$ by an I_d process that is not sensitive to the nature of L. It can also react directly to form $[\mathrm{Ru_3(CO)_{12}}]$ by a process similar to those in equations (8) and (10).

On the other hand, the values of *a* in saturated non-co-ordinating hydrocarbons do most probably correspond to k_2/k_1 and provide relative values for nucleophilic attack by L on the vacant co-ordination site in $[\mathrm{Ru_3(CO)_{12}}]^{**}$. These suggest that steric effects are determining since $\mathrm{PPh_3}$ is more basic but larger than $\mathrm{P(OPh)_3}$, $\mathrm{PPh_3}$ is of about the same basicity as $\mathrm{P(OMe)_3}$ but much larger, and CO is a weakly basic nucleophile but very small.[16,17] This implies that the vacant co-ordination site in $[\mathrm{Ru_3(CO)_{12}}]^{**}$ is sterically quite inaccessible.

Photofragmentation of $[\mathrm{Ru_3(CO)_9L_3}]$.—The cluster $[\mathrm{Ru_3(CO)_9(PPh_3)_3}]$ undergoes photofragmentation with $\mathrm{PPh_3}$ at 436 nm with a very low efficiency in benzene. The $[\mathrm{PPh_3}]$-independent quantum yield, φ(lim.), is essentially the same as the value of φ(obs.) for photofragmentation with CO at 405 nm in cyclohexane.[2] It is not clear whether the low efficiency is due to photophysical effects on φ(max.) or to a low value of a partition ratio such as $k_4/(k_4 + k_6)$ for thermal reactions of a reactive intermediate. Since it is the value of φ(lim.) that is low the low value cannot be due to a low value of the ratio k_2/k_1 as suggested by Ford and co-workers[2] on the basis of studies of photolysis with CO in which it was not established whether a limiting quantum yield had been reached or not. The low quantum yield must be due either to a much lower value of φ(max.) for $[\mathrm{Ru_3(CO)_9(PPh_3)_3}]$ or to a much larger value of k_6/k_4.

Reaction with $\mathrm{PPh_3}$ at 313 nm is considerably more efficient than at 405 or 436 nm, though it is still much less efficient than reaction of $[\mathrm{Ru_3(CO)_{12}}]$ at 436 nm. The data conform to equation (1) and competitive reactions of a reactive intermediate are implied. The much greater value of φ(lim.) at 313 nm than at 405 or 436 nm suggests that different intermediates are involved although photofragmentation is still the ultimate reaction. The question of whether this wavelength dependence is related to a reversal of the excited-state order in $[\mathrm{Ru_3(CO)_9(PPh_3)_3}]$ compared with $[\mathrm{Ru_3(CO)_{12}}]$ is still open.[2,18] The competition ratio, k_2/k_1, for irradiation at 313 nm in benzene (Table 4) is much larger than the corresponding ratio for $[\mathrm{Ru_3(CO)_{12}}]$ at 436 nm, *i.e.* the reactive intermediate produced from $[\mathrm{Ru_3(CO)_9(PPh_3)_3}]$ is relatively much more susceptible to attack by $\mathrm{PPh_3}$ than it is to reversion to stable $[\mathrm{Ru_3(CO)_9(PPh_3)_3}]$ in spite of presumably less favourable steric effects.

The behaviour of $[\mathrm{Ru_3(CO)_9(PBu^n{}_3)_3}]$ on excitation at 366 nm is different. Two intermediates seem to be involved, one that undergoes fragmentation with rates that are decreased by increasing $[\mathrm{PBu^n{}_3}]$ and another that undergoes $[\mathrm{PBu^n{}_3}]$-independent fragmentation (when $[\mathrm{PBu^n{}_3}] \gtrsim 0.02$ mol $\mathrm{dm^{-3}}$). This latter path is retarded by CO and it is possible that the two paths are dissociative, one involving $\mathrm{PBu^n{}_3}$ dissociation and the other CO dissociation.

These preliminary results for photolysis of substituted $\mathrm{Ru_3}$ clusters show enough interesting features for further studies to be fully justified.

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* The value of φ(lim.) for 1-octene is *ca.* 2 times that for $\mathrm{P(OMe)_3}$ for $[\mathrm{Ru_3(CO)_{12}}]$ whereas it is *ca.* 70% of that for $\mathrm{P(OEt)_3}$ for $[\mathrm{Os_3(CO)_{12}}]$.[8] This difference may arise from the fact that the photolysis of $[\mathrm{Ru_3(CO)_{12}}]$ leads to fragmentation with both nucleophiles whereas photolysis of $[\mathrm{Os_3(CO)_{12}}]$ leads to fragmentation with 1-octene but to substitution with $\mathrm{P(OEt)_3}$.

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