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Photosensitized Initiation of Polymerization of Methyl Methacrylate by Triosmium Dodecacarbonyl

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PHOTOSENSITIZED INITIATION OF POLYMERIZATION OF METHYL METHACRYLATE BY TRIOSMIUM DODECACARBONYL

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ABSTRACT

The kinetic study of the mechanism of photosensitized initiation of methyl methacrylate (MMA) polymerization by $Os_3(CO)_{12}/CCl_4$ at $\lambda = 365$ nm is presented. The monomer is found to participate in the initiation process. Observed initiation by $Os_3(CO)_{12}$/MMA is explained in the light of a hydrogen abstraction process and $Os_3(CO)_{12}/CCl_4$/MMA as an electron transfer process. The ratio of the rate constants of the component reactions were evaluated. The observed values of the kinetic parameter $k_p k_t^{-1/2}$ demonstrate that retardation does not occur in these reactions. The quantum yield of photoinitiation of $Os_3(CO)_{12}/CCl_4$/MMA is significantly low, i.e., ~0.013 as compared to that of other metal carbonyls such as $Mn_2(CO)_{10}/CCl_4$/MMA and $Re_2(CO)_{10}/CCl_4$/MMA, where the quantum yield of initiation is reported to be close to unity.

INTRODUCTION

Metal carbonyls of Group VIIA are well known to be effective photosensitizers for the initiation of vinyl polymerization in the presence of a

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suitable organic halide [1-6]. In these processes, the metal assumes a higher oxidation state and the halide generally splits into an anion and a radical fragment. For example, if M^0 represents a metal in the zero oxidation state, and carbon tetrachloride is the organic halide, then the reaction can be presented as

$$M^0 + CCl_4 \rightarrow M^+Cl^- + \cdot CCl_3$$

It is found that the initial rate of polymerization increases as the concentration of halide increases at a constant absorbed intensity. The rate finally reaches a limiting value, showing that further addition of CCl_4 has no significant effect on the rate. In the absence of halides, $Mn_2(CO)_{10}$ is ineffective with common vinyl monomers, but $Re_2(CO)_{10}$ and $Os_3(C)_{12}$ give rise to relatively slow photoinitiation which has been attributed to hydrogen abstraction [7].

The quantum yields for the photoinitiation of $Mn_2(CO)_{10}$ at a limiting CCl_4 concentration were found to be close to unity with a variety of monomers [2]. With $Re_2(CO)_{10}/CCl_4$/MMA for short reaction times ($\lambda = 365$ nm), the quantum yield was also close to unity [4]. In these systems, therefore, each quantum absorbed leads to one initiating radical.

Bamford et al. investigated a variety of monomer systems in detail and proposed that the photoinitiation of free radical polymerization sensitized by transition metal carbonyls proceeded by at least three routes: 1) electron transfer to an organic halide with the rupture of a C—Cl or C—Br bond, 2) reaction with a strong electron-attracting monomer such as C_2F_4 without rupture of C—F to form an initiating radical, and 3) hydrogen atom transfer from a monomer or a solvent to a photoexcited metal carbonyl species [8].

In this paper the kinetics and mechanism of the photosensitized initiation of the free radical polymerization of methyl methacrylate by $Os_3(C)_{12}$ alone and $Os_3(CO)_{12}/CCl_4$ are presented. It was found that the photoinitiation of polymerization of vinyl monomers by $Os_3(CO)_{12}$ without a halide occurs primarily by hydrogen abstraction, whereas initiation with an organic halide predominantly occurs by electron transfer to the organic halide. The observed quantum yield of initiation in an $Os_3(CO)_{12}/CCl_4$/MMA initiated system is unusually low compared to the $Mn_2(CO)_{10}/CCl_4$/MMA and $Re_2(CO)_{10}/CCl_4$/MMA systems [2, 4].

EXPERIMENTAL

All experiments were carried out in inactive sodium light to avoid complications from undesirable photochemical reactions.

The polymerization reactions were performed either inside a dilatometer or in a gravimetric tube. In each case, oxygen was excluded from the reaction mixture by the use of a high vacuum (10^{-6} mmHg) system. Degassing of the reaction mixture involved freezing and thawing under vacuum about 6–8 times. The reactants were then frozen in liquid nitrogen and kept open to the pumping system while the reaction vessel was sealed off by an oxygen flame at the constriction.

The optical system consisted of a high pressure mercury arc vapor lamp (Mazda 250 W Type ME/D) and two quartz lenses placed on an optical bench. The position of the lamp was kept fixed while the two lenses were adjusted to produce a parallel beam of light. This light was then transmitted through a glass filter (Chance OVI glass filter, 3-in. diameter) which essentially gives monochromatic light of wavelength 365 nm. Calibration of the filter in a Unican SP 800 spectrophotometer suggests the transmitted light was predominantly of wavelength 365 nm. The uniformity and approximate intensity of the light was repeatedly measured by using a light meter consisting of a cadmium sulfide photocell and a moving coil meter.

In the case of dilatometry, the initial rates of polymerization were measured with the aid of a cathetometer by following the contraction in volume of the reaction mixture with time. The reaction mixture was exposed to light after thermal equilibrium was reached.

A plot of contraction (centimeters) against time (minutes) gave the contraction R (cm·min^{-1}·mL of dilatometer·vol^{-1}). The rate of polymerization ω was then calculated from

$$\omega = KR \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \qquad (1)$$

where $K = 5.06 \times 10^{-3}$ mol·L^{-1}/cm·min^{-1}·vol^{-1} for the methyl methacrylate monomer at 25°C.

The evolution of carbon monoxide was determined by the use of a Töpler pump with an attached gas burette. The noncondensable gas, CO, was pumped into the gas burette where its volume was measured.

Gas chromatographic measurements were carried out with the help of a Pye Unicam Gas Liquid Chromatograph with dual flame ionization detectors by using a 2-m long silcone column containing 5% silicone on Embacel, 60–100 mesh acid washed. The column was used at 150°C, and the sample was injected at room temperature. Nitrogen was used as the carrier gas. The products were detected by comparing the retention time with authentic samples. The peaks were recorded on a Honeywell pen recorder.

Infrared spectra were recorded on a Unicam SP 200 and a Perkin-Elmer 257 Grating Infra-red Spectrophotometer.

Materials

Methyl methacrylate (MMA), obtained from Hopkin and Williams Ltd., contained hydroquinone as an inhibitor. The inhibitor was removed by washing the MMA several times with 10% (w/v) sodium hydroxide and distilled water. It was then dried over anhydrous calcium chloride, fractionally distilled under reduced pressure (bp 46°C/100 mm Hg of N_2), and the middle fraction was collected. Finally, it was prepolymerized by saturating it with $Os_3(CO)_{12}$ and irradiating it for 6 h. The residual monomer was distilled under vacuum before use.

Carbon tetrachloride (Analar grade) was stored in the dark and was used without further purification. Diphenyl, dibenzyl, and bicyclohexyl were used without further purification. Cyclohexane (Hopkin and Williams) was thoroughly shaken with concentrated sulfuric acid. It was then washed in sodium hydroxide followed by water to remove traces of alkali. The cyclohexane thus obtained was dried overnight on calcium hydride, and the middle fraction was collected from distillation. Spectrosol cyclohexane used without further purification made no difference in the results.

Osmium carbonyl, $Os_3(CO)_{12}$, was received as a gift from ICI Ltd. Subsequently, it was procured from Strem Chemicals, Inc., USA, stored in the dark, and used without further purification. Manganese carbonyl was purified by subliming at room temperature at a pressure of 10^{-4} mmHg and stored in the dark. Rehenium carbonyl, received as a gift from ICI, was used without further purification.

RESULTS AND DISCUSSION

Absorption Spectra

Osmium carbonyl absorbs quite strongly at a wavelength of 365 nm. The concentrations of the carbonyl employed for photoinitiation were therefore limited and the absorption of the incident light was maintained

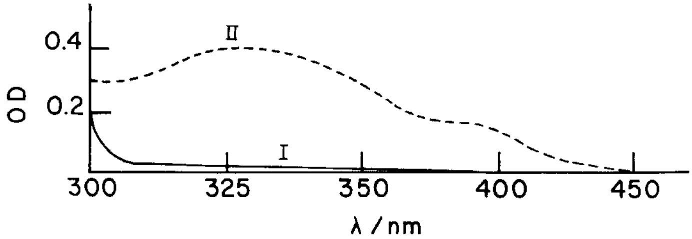

FIG. 1. Ultraviolet absorption spectra. I: Methyl methacrylate. II: $[Os_3(CO)_{12}] = 4.2 \times 10^{-5}$ mol/L in MMA. Path length = 10 mm.

in most cases below 30%. Such an arrangement ensured a sensibly uniform reaction throughout the medium. Experiments at longer wavelengths, for example, at 435.8 nm, where the absorption was much less (Fig. 1, Curve I), failed to give an appreciable rate of polymerization. MMA absorbs a small amount of light at $\lambda = 365$ nm (Fig. 1, Curve II), thus a rate of polymerization of $1.3 \times 10^{-5}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ is observed when MMA is placed in a light beam of intensity $2.0 \times 10^{-6}\ \text{ein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ in the absence of catalyst. Hence, a correction was made by using the relation

$$\omega = (\omega_T^2 - \omega_0^2)^{1/2} \tag{2}$$

where ω is the corrected rate of polymerization, and ω_T and ω_0 represent the overall catalyzed polymerization and uncatalyzed polymerization, respectively. Systems containing MMA/$Os_3(CO)_{12}$ or MMA/$Os_3(CO)_{12}$ + halide in the reaction mixture do not give an appreciable rate of polymerization in the dark at 25°C.

Determination of the Kinetic Parameter $k_p k_t^{-1/2}$ at 25°C.

The kinetic parameter $k_p k_t^{-1/2}$ for methyl methacrylate polymerization was determined from the gravimetric rate of polymerization, ω, and the kinetic chain length $\bar{\nu}$, by use of

$$k_p k_t^{-1/2} = [M]^{-1}(\omega\bar{\nu})^{1/2} \tag{3}$$

The kinetic chain length was estimated from the number-average molecular weights by the use of

TABLE 1. Values of $k_pk_t^{-1/2}$ for the Photopolymerization of MMA at 25 °C at Varying $Os_3(CO)_{12}$ Concentration; Reaction Mixture Irradiated at λ = 365 nm; $[CCl_4] = 1.03 \times 10^{-1}$ mol/L

$10^5[Os_3(CO)_{12}]$, mol/L	Irradiation period, min	$10^5\omega$, mol·L^{-1}·s^{-1}	$10^{-3}\bar{P}_n$	$10^{-3}\bar{\nu}$	$k_pk_t^{-1/2}$ ·mol$^{-1/2}$·L$^{1/2}$·s$^{-1/2}$
9.6	14	7.62	4.169	2.482	0.055
7.2	15	6.77	4.786	4.005	0.056
3.6	20	4.36	6.448	5.460	0.053
1.8	30	3.11	9.960	8.317	0.054
1.2	30	2.72	13.183	11.225	0.059

$$\bar{\nu} = \bar{P}_n \frac{(2 + y)}{2(1 + y)} \tag{4}$$

where $y = 0.47$ [9]. Equation (4) allows for the occurrence of both combination and disproportionation in the termination reaction of MMA at 25 °C.

In Table 1 the degree of polymerization is not corrected for chain transfer to monomer and halide. Both carbon tetrachloride and methyl methacrylate have very low transfer constants at 25 °C, and correction makes insignificant changes in $\bar{P}_n$ values. These results agree well with the literature value for an unretarded free radical polymerization initiated by the conventional initiator AIEN ($k_pk_t^{-1/2} = 0.055$ mol$^{-1/2}$·L$^{1/2}$·s$^{-1/2}$) at 25 °C [2, 10]. Therefore, the values of $k_pk_t^{-1/2}$ shown in Table 1 support the fact that retardation does not occur in these reactions.

Dependence of Rate on Carbon Tetrachloride Concentration

The rate of initiation as a function of carbon tetrachloride concentration, [H], is presented in Fig. 2. The rate of initiation is calculated from the rate of polymerization by employing

$$\omega = k_pk_t^{-1/2}[M][J]^{1/2} \tag{5}$$

where $k_p k_t^{-1/2} = 0.055\ \text{mol}^{-1/2}\cdot\text{L}^{1/2}\cdot\text{s}^{-1/2}$.

The rate of initiation increases initially with an increase of $[\text{CCl}_4]$ and finally reaches to limiting rate, showing that further addition of carbon tetrachloride has very little effect on the rate of polymerization. It is interesting to note that a genuine rate of initiation is observed in the absence of halide. The increase of initiation of polymerization in the $\text{Os}_3(\text{CO})_{12}/\text{CCl}_4/\text{MMA}$ system is about 2.5-fold from $[\text{CCl}_4] = 0$ to the limiting $[\text{CCl}_4]$. The increment in rate is only moderate compared to other systems previously studied [2]. The rate becomes independent at about $[\text{CCl}_4] = 2.0 \times 10^{-3}$ mol/L. The dependence of the rate of polymerization and the rate of initiation on the variation of $[\text{CCl}_4]$ can be represented by

$$\omega = 3.69 \times 10^{-4}\left[\frac{[\text{H}] + 10^{-4}}{[\text{H}] + 2.5 \times 10^{-4}}\right]^{1/2} \tag{6}$$

$$J = 5.09 \times 10^{-9}\left[\frac{[\text{H}] + 10^{-4}}{[\text{H}] + 2.5 \times 10^{-4}}\right] \tag{7}$$

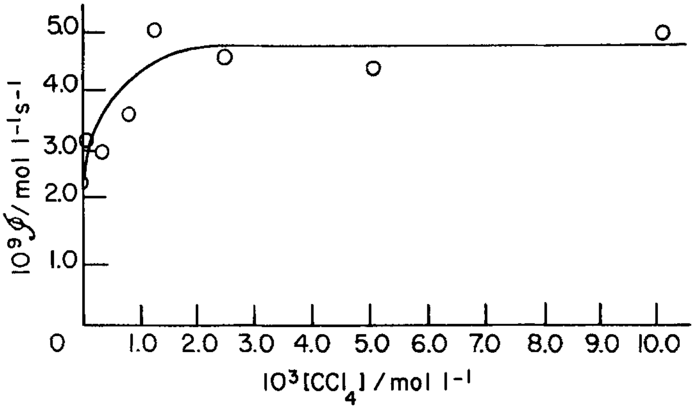

FIG. 2. Dependence of the initial rates of initiation on carbon tetrachloride concentration at 25°C. Monomer = MMA, $[\text{Os}_3(\text{CO})_{12}] = 2.1 \times 10^{-5}$ mol/L. $I_0 = 1.95 \times 10^{-6}\ \text{ein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$. Curve calculated from Eq. (14) with the aid of kinetic parameters given in Table 9.

TABLE 2. Comparison of the Rate of Photopolymerization of MMA at 25 °C by Metal Carbonyls without Organic Halide; Irradiated at λ = 365 nm

Carbonyl	Initiator concentration, mol/L	Rate of polymerization, $mol \cdot L^{-1} \cdot s^{-1}$
$Mn_2(CO)_{10}$	8.5×10^{-4}	No measurable rate
$Re_2(CO)_{10}$	2.8×10^{-4}	1.58×10^{-5}
$Os_3(CO)_{12}$	7.2×10^{-5}	2.57×10^{-5}

It can be seen that at high concentrations of halide, the term in brackets of Eq. (6) and (7) approaches unity and the rate of polymerization ultimately assumes a limiting value.

Polymerization of MMA without Organic Halide

MMA purified by standard methods was further scavanged by $Os_3(CO)_{12}$, including polymerization, by adopting the process mentioned in the Experimental Section. The monomer thus obtained after vacuum distillation gave results identical to those shown in Fig. 2. Similar experiments using $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ with methyl methacrylate in the absence of halide were carried out. The results are given in Table 2.

The rate of polymerization in Table 2 was corrected by using Eq. (2). A correction for the thermal rate makes very little change in the rate of polymerization since the thermal rate was very small. The values quoted in Tables 2 and 4 are lower than that in Fig. 2. This is caused by the difference in incident light intensity.

Evidence of Hydrogen Abstraction Reaction

Metal carbonyls such as $Os_3(CO)_{12}$, $Re_2(CO)_{10}$, and $Mn_2(CO)_{10}$ were irradiated for about 60 h at λ = 365 nm in cyclohexane solution. All these carbonyls gave rise to the formation of bicyclohexyl, identified by gas-liquid chromatography. These experiments, as we reported previously, are consistent with hydrogen abstraction from cyclohexane by the photoexcited species, leading to cyclohexyl radicals which subsequently dimerize [7].

TABLE 3. Infrared Bands (cm^{-1}) of Carbonyl Products Isolated from the Reaction Mixture

i) Osmium carbonyl irradiated in cyclohexane and measured in cyclohexane.
Hydride mixture 2015s, 2025w, 2040vs, 2055m, 2060s, 2080vs.
ii) Osmium carbonyl irradiated in cumene and products measured in cumene.
Hydride mixture 2025vs, 2035s, 2070vs, 2075vw, 2085vs.
iii) Osmium carbonyl irradiated in toluene and products measured in toluene.
Hydride mixture 2015s, 2025w, 2038vs, 2050w, 2060w, 2070vs.
iv) Osmium carbonyl measured in cyclohexane.
$Os_3(CO)_{12}$ 1990w, 2010w, 2030vs, 2065vs.

The infrared spectrum of the mixture was then compared with that of the osmium products obtained by the irradiation of $Os_3(CO)_{12}$ in cyclohexane after removal of all volatile products in vacuum. The bands due to the hydride mixture are shown in Table 3-i; bands present in $Os_3(CO)_{12}$ are not shown in 3-i, 3-ii, and 3-iii.

It was thought that if a hydrogen abstraction process is operative, the addition of a compound containing labile hydrogen to a reaction mixture containing $Os_3(CO)_{12}$ and MMA might increase the polymerization rate. This was found to be true. Upon the addition of cumene, $v_a = 0.3$, the rate of initiation increased to approximately twice that obtained in bulk MMA. The result is presented in Table 4. The rate of initiation in Table 4 is calculated by using a $k_p k_t^{-1/2}$ value of 0.055 $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$.

The infrared spectrum of the irradiation products of $Os_3(CO)_{12}$ in cumene, after removal of all volatiles, shows the bands given in Table

TABLE 4. Photopolymerization of MMA at 25°C; Irradiated at $\lambda = 365$ nm; $[Os_3(CO)_{12}] = 5.5 \times 10^{-5}$ mol/L, volume fraction of cumene $v_a = 0.3$

System	$10^5 \omega$, $mol \cdot L^{-1} \cdot s^{-1}$	$10^9 J$, $mol \cdot L^{-1} \cdot s^{-1}$
MMA + $Os_3(CO)_{12}$	2.39	2.15
MMA + $Os_3(CO)_{12}$ + cumene	2.51	4.75

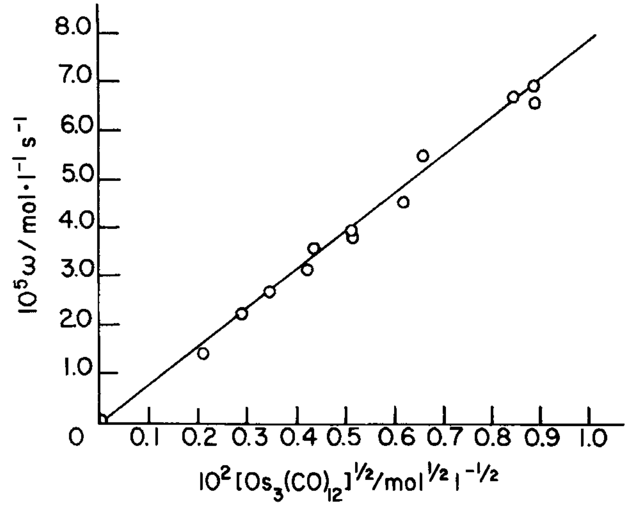

FIG. 3. Initial rates of polymerization of MMA as a function of $[Os_3(CO)_{12}]$ at 25°C (λ = 365 mm). $I_0 = 1.95 \times 10^{-6}$ ein·L^{-1}·s^{-1}, $[CCl_4] = 1.03 \times 10^{-1}$ mol/L.

3-ii. The irradiation was carried out for a period of 70 h. Similar experiments with $Os_3(CO)_{12}$ in toluene with irradiation for 60–70 h and subsequent stripping off of the volatile products gave rise to the bands presented in Table 3-iii.

The infrared spectrum of the products from $Os_3(CO)_{12}$ in cumene appears to be different from those of the $Os_3(CO)_{12}$ products in cyclohexane and in toluene. However, all the bands shown in Table 3 are present in the hydride mixture obtained by Lewis et al. [11].

These experiments suggest that the photoinitiation of polymerization by carbonyls in the absence of halide can occur through hydrogen abstraction from the monomer [7].

Dependence of the Rate of Polymerization on Carbonyl Concentration

A plot of the rate of polymerization of methyl methacrylate against the square root of $[Os_3(CO)_{12}]$ at constant $[CCl_4]$ is shown in Fig. 3. The rate of polymerization ω here refers only to photosensitized polymerization of MMA at 25°C by $Os_3(CO)_{12}$, ω being obtained from Relation (2), assuming $k_p k_t^{-1/2} = 0.055\ \text{mol}^{-1/2}\cdot\text{L}^{1/2}\cdot\text{s}^{-1/2}$. The linear dependence of ω–$[\text{Os}_3(\text{CO})_{12}]^{1/2}$, as can be seen in Fig. 3, holds good over the whole range of concentrations that was employed. This observation suggests that no retardation or inhibition is encountered. Retardation or inhibition would lead to departure from the square-root relationship. The rate of polymerization and initiation at $I_0 = 1.95 \times 10^{-6}\ \text{ein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ is given by

$$\omega = 7.89 \times 10^{-3}[\text{Os}_3(\text{CO})_{12}]^{1/2}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \tag{8}$$

$$J = 2.4 \times 10^{-4}[\text{Os}_3(\text{CO})_{12}]\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \tag{9}$$

Equations (8) and (9) are consistent with the idea that initiation of polymerization of MMA with $\text{Os}_3(\text{CO})_{12}$ involves free-radical intermediates, as postulated previously for reactions initiated by other Group VII-A carbonyls + organic halide systems [2, 4].

Dependence of the Rate of Polymerization on Intensity of the Absorbed Light

Figure 4 shows a plot of the rate of polymerization against the square root of the absorbed light intensity, $I_{\text{abs}}^{1/2}$, at constant $[\text{Os}_3(\text{CO})_{12}]$ and $[\text{CCl}_4]$. The rate of photosensitized polymerization of MMA is proportional to $I_{\text{abs}}^{1/2}$ and can be expressed by

$$\omega = 2.93 \times 10^{-2}\, I_{\text{abs}}^{1/2}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \tag{10}$$

These results, i.e., ω–$[\text{Os}_3(\text{CO})_{12}]^{1/2}$, ω–$I_{\text{abs}}^{1/2}$ dependence, and the value of $k_p k_t^{-1/2}$, are consistent with the idea that the process of photosensitized polymerization of MMA by $\text{Os}_3(\text{CO})_{12}$ is free radical in nature.

Dependence of Rate on [CCl$_4$] at $P_{\text{CO}} = 100$ mmHg

The polymerization of MMA at different $[\text{CCl}_4]$ in the presence of CO at 100 mmHg was carried out gravimetrically. Results showing the average gravimetric rate are given in Table 5. The rate of polymerization in the absence and presence of carbon tetrachloride at constant light intensity and $[\text{Os}_3(\text{CO})_{12}]$ is almost unaffected by the addition of 100 mmCO. The nature and sharpness of the ω–$[\text{CCl}_4]$ curve remains unaltered. This eliminates the involvement of carbon monoxide in the rate-

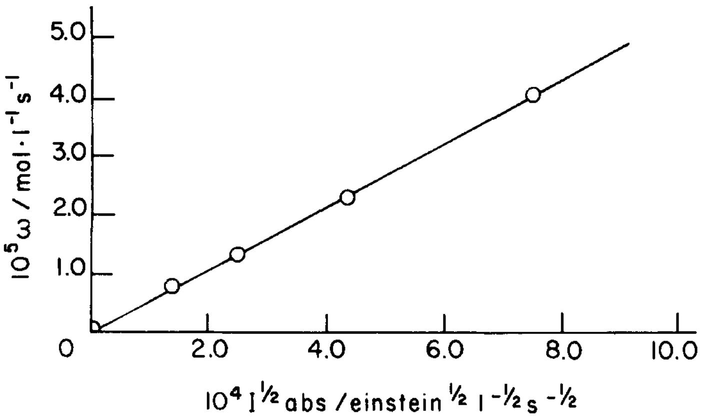

FIG. 4. Dependence of the initial rates of polymerization of MMA on the square root of the intensity of the absorbed light at 25°C. $[Os_3(CO)_{12}] = 2.65 \times 10^{-5}$ mol/L, $[CCl_4] = 1.03 \times 10^{-1}$ mol/L.

TABLE 5. Dependence of the Rate of Photopolymerization on $[CCl_4]$ With and Without Carbon Monoxide; $[Os_3(CO)_{12}] = 4.4 \times 10^{-5}$ mol/L; irradiated at $\lambda = 365$ nm

Experiment	$10^3[CCl_4]$, mol/L	Irradiation period, min	CO added	$10^5\omega$, mol·L^{-1}·s^{-1}
M1	0.00	65	None	2.5
M2	0.00	65	100 mm	2.5
M3	0.30	40	None	3.71
M4	0.30	40	100 mm	3.55
M5	3.0	40	None	4.25
M6	3.0	40	100 mm	4.11
M7	6.0	40	None	4.54
M8	6.0	40	100 mm	4.32
M9	101.0	40	None	4.70
M10	101.0	50	100 mm	4.53

determining step. Photopolymerizations of MMA with $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ show a similar effect [2, 4].

Evolution of Carbon Monoxide

Experiments were carried out to determine the number of carbon monoxide ligands liberated from the carbonyl during the course of reaction. Reaction mixtures containing $Os_3(CO)_{12}$ in methyl methacrylate and CCl_4 were irradiated at $\lambda = 365$ nm for certain periods. The quantity of carbon monoxide evolved was measured by the use of a Töpler pump.

In order to compare the rates of initiation and evolution of carbon monoxide, the polymer formed during the period of irradiation was precipitated in methanol by adopting the procedure discussed in the Experimental Section. The rate of initiation was then calculated from the average rate of polymerization by using Eq. (5). It was found that the number of CO molecules evolved by the decomposition of each molecule of $Os_3(CO)_{12}$ is approximately 1.4.

Irradiation of $Os_3(CO)_{12}$ in MMA, in the absence of halide, also liberated CO. The amount of CO evolved was almost the same as in the $Os_3(CO)_{12}/CCl_4/MMA$ system. This implies that in subsequent steps where carbon tetrachloride is reduced by the photoactive species, no further evolution of carbon monoxide occurs. The displacement of the ligand CO from the metal carbonyl takes place in an earlier step. Evolution of carbon monoxide also occurs when $Os_3(CO)_{12}$ is irradiated in benzene. The rate of evolution of CO in $MMA/Os_3(CO)_{12}$ and $MMA/Os_3(CO)_{12}/CCl_4$ systems are of the same order, approximately $1.5 \times 10^{-6}\ mol \cdot L^{-1} \cdot s^{-1}$.

Dependence of Rate of Polymerization on Monomer Concentration

A log plot of the rate of polymerization against log [M] is shown in Fig. 5. The order in monomer for photosensitized polymerization at a high halide content is 1.32 with benzene as diluent. Normally, in a free-radical polymerization reaction when monomer is not involved in the initiation process, an order of unity is expected. It appears from this result that monomer must be playing a role in the initiating system. Although the velocity of the termination coefficient is dependent on the viscosity of the medium, no correction for viscosity has been made since the viscosity of benzene is very close to that of the monomer [12].

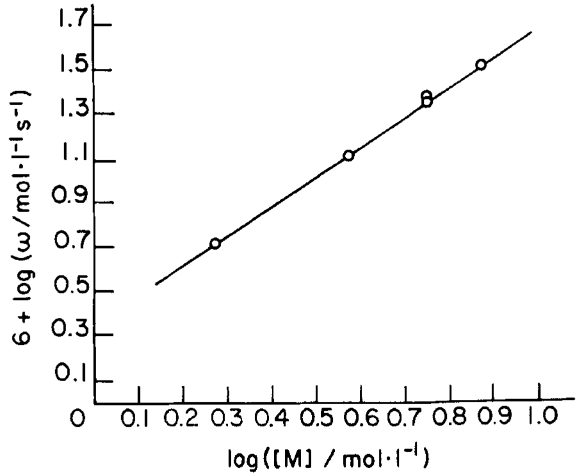

FIG. 5. Photosensitized rates of polymerization of MMA as a function of monomer concentration. $[Os_3(CO)_{12}] = 2.65 \times 10^{-5}$ mol/L, $[CCl_4] = 1.03 \times 10^{-1}$ mol/L, $I_0 = 1.96 \times 10^{-6}$ ein·L^{-1}·s^{-1}. Benzene is used as diluent.

Quantum Yields of Initiation

The quantum yield of initiation, ϕ_i, was calculated from the expression

$$\phi_i = \phi_0/\bar{\nu} \tag{11}$$

where $\phi_0 = \omega/I_{abs}$ and ϕ_0 represents the overall quantum yield. The intensity of the incident light beam was determined by irradiating a potassium ferrioxalate solution in a dilatometer bulb ($\lambda = 365$ nm) at 25°C, following the method designed by Hatchard and Parker [13]. The rate of polymerization was measured by irradiating the reaction mixture in the same dilatometer under identical conditions. I_{abs} is calculated from knowledge of the incident quantum input.

Quantum yields of initiation, ϕ_i, for MMA/$Os_3(CO)_{12}$/CCl_4 systems are presented in Table 6. The low quantum yield of initiation, $\phi i \approx 0.013$, means that most of the absorbed light does not bring about the decomposition of the $Os_3(CO)_{12}$ to give rise to initiation.

TABLE 6. Quantum Yields of Initiation for the Polymerization of MMA at Limiting Halide Concentration. $[CCl_4] = 1.03 \times 10^{-1}$ mol/L and $I_0 = 1.95 \times 10^{-6}$ ein·L^{-1}·s^{-1}

$10^5[Os_3(CO)_{12}]$, mol/L	$10^7 I_{abs}$, ein·L^{-1}·s^{-1}	$10^5\omega$, mol·L^{-1}·s^{-1}	$10^9 J$, mol·L^{-1}·s^{-1}	$10^4\bar{\nu}$	ϕ_0	ϕ_i
2.65	5.53	4.3	6.9	0.623	77.7	0.0124
3.68	6.57	4.8	8.8	0.550	73.6	0.0130

Determination of the Number of Radicals Generated from the Decomposition of Each Molecule of Initiator

The number of radicals, n, is estimated from the decrease of initiator concentration corresponding to conversion, ΔM, at a given time interval. Measurements of ΔM as a function of reaction time were made dilatometrically, and the results were fitted in Eq. (12) with the aid of a program which minimizes the standard deviation:

$$\Delta h = \beta \int_0^t (Ae^{-k_c t} + 1)^{1/2} dt \qquad (12)$$

where Δh (cm) is the change in meniscus level of the dilatometer capillary corresponding to the conversion ΔM (mol/L).

If V (mL) is the dilatometer volume and the capillary has an internal diameter of 1 mm, then for MMA at 25 °C:

$$\beta = 0.304\omega_0/V$$

$$A = k_c n C_0 J_0$$

The time-conversion curves at varying $[Os_3(CO)_{12}]$ calculated from Eq. (12) are shown in Fig. 6. The values of k_c and n obtained from these curves are presented in Table 7.

Polymerization of Styrene with $Os_3(CO)_{12}$ in the Presence of CCl_4

A known concentration of initiator solution was made up by dissolving $Os_3(CO)_{12}$ in benzene. Equal amounts of the initiator solution were then added to MMA/CCl_4 and St/CCl_4 mixtures. The degassed reaction mixtures were then irradiated in dilatometers under identical experimental condition. The rate of polymerization of both monomers is shown in Table 8.

Mechanism of Initiation

The main observations can be summarized as follows: 1) A significant rate of initiation occurs in the absence of halide. 2) The rate of polymerization is proportional to $[Os_3(CO)_{12}]^{1/2}$. 3) The rate of polymerization is dependent on the square root of the absorbed light intensity. 4) The rate of polymerization increases with an increase of halide concentration,

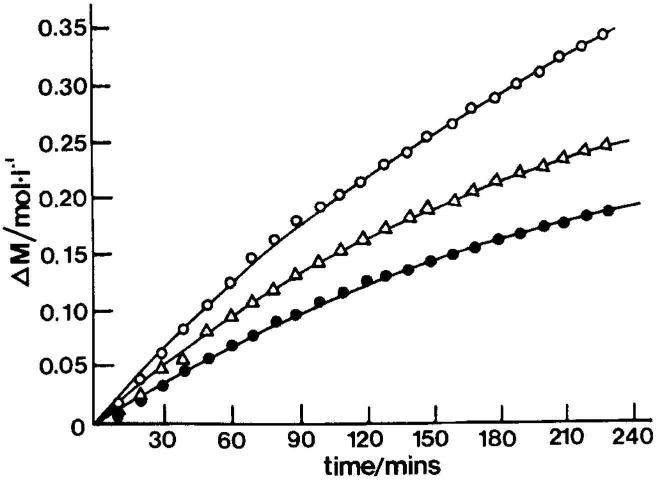

FIG. 6. Conversion as a function of reaction time at 25°C Irradiated at λ = 365 nm. [$Os_3(CO)_{12}$]: (○) 5.88 × 10^{-5} mol/L, (△) 2.94 × 10^{-5} mol/L, (●) 1.47 × 10^{-5} mol/L, [CCl_4] = 1.03 × 10^{-1} mol/L, I_0 = 1.01 × 10^{-6} ein·L^{-1}·s^{-1}.

finally reaching a plateau value; further addition of halide at this stage does not increase the rate. 5) The order in monomer is 1.3 when benzene is used as diluent. 6) The rate of polymerization is not affected when CO is added to the system. 7) Evolution of carbon monoxide is observed when $Os_3(CO)_{12}$/MMA, $Os_3(CO)_{12}$/MMA/CCl_4, and $Os_3(CO)_{12}$/benzene are irradiated. 8) At a high halide concentration, the initiating radical is $^{\cdot}CCl_3$ or $^{\cdot}CCl_3M$. 9) The number of radicals formed from the decompo-

TABLE 7. Number of Radicals Generated from the Decomposition of Each Molecule of Initiator. [CCl_4] = 1.03 × 10^{-1} mol/L and I_0 = 1.01 × 10^{-6} ein·L^{-1}·s^{-1}

10^5[$Os_3(CO)_{12}$], mol/L	$10^4 k_c$, s^{-1}	n
1.47	1.63	0.70
2.94	1.53	0.61
5.88	1.50	0.65

TABLE 8. Photopolymerization of MMA and Styrene at 25°C with $Os_3(C))_{12}$; $[CCl_4] = 1.03 \times 10^{-1}$ mol/L; $[Os_3(CO)_{12}] = 6.9 \times 10^{-5}$ mol/L; irradiated at $\lambda = 365$ nm

Monomer [M]	[M], mol/L	$10^5\omega$, $mol \cdot L^{-1} \cdot s^{-1}$	$k_p k_t^{-1/2}$, $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$	$10^8 J$, $mol \cdot L^{-1} \cdot s^{-1}$
MMA	4.47	6.5	0.054	6.32
St	4.36	4.76	0.0083	1.7

sition of a carbonyl molecule is close to unity. 10) Quantum yields for photodecomposition are very low. 11) Photoinitiation of MMA and styrene does not proceed at the same rate; initiation of MMA is faster than of styrene. On the basis of the experimental observations, the following mechanism is proposed.

$$Os_3(CO)_{12} + h\nu \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(Os^*)}{Os_3(CO)_{12}^*} \tag{13a}$$

$$Os^* + M \xrightarrow[k_3]{} \underset{(I)}{Os_3(CO)_{12} \ldots M^*} \tag{13b}$$

$$I \xrightarrow{k_d} Os_3(CO)_{12} + M \tag{13c}$$

$$I \xrightarrow[k_4]{} \underset{(II)}{OS_3(CO)_{11} - M} + (CO) \tag{13d}$$

$$II + CCl_4 \xrightarrow[k_5]{} CCl_3M^{\cdot} + \tag{13e}$$

$$II \xrightarrow[k_6']{} M^{\cdot} \tag{13f}$$

$$II \xrightarrow[k_7']{} \text{inactive products} \tag{13g}$$

Assuming a steady-state concentration of the intermediates, Os*, I, and II, and supposing all the $^{\cdot}CCl_3$ or $^{\cdot}CCl_3M$ radicals produced initiate polymerization, the rate of initiation, J, is given by

$$J = \frac{\{k_1[\mathrm{Os_3(CO)_{12}}][\mathrm{M}]I_0\}\{[\mathrm{H}] + (k_6'/k_5)\}}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}[\mathrm{H}] + (k_6'/k_5) + (k_7'/k_5)\}} \tag{14}$$

and the rate of polymerization, ω, is given by

$$\omega = k_1^{1/2}k_p k_t^{-1/2}[\mathrm{M}][\mathrm{Os_3(CO)_{12}}]^{1/2}[\mathrm{I_0}]^{1/2} \tag{15}$$

$$\left[\frac{\{[\mathrm{H}] + (k_6'/k_5)\}/\{[\mathrm{H}] + (k_6'/k_5) + (k_7'/k_5)\}}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}}\right]^{1/2}$$

The rate of initiation at $[\mathrm{CCl_4}] = 0$ is given by Eq. (16). The variations of the rate of initiation with $[\mathrm{CCl_4}]$, given by Eq. (17) and (18), are of the correct form. The rate initially increases with the addition of halide,

$$J = \frac{k_1[\mathrm{Os_3(CO)_{12}}][\mathrm{M}]I_0\{(k_6'/k_5)\}/\{(k_6'/k_5) + (k_7'/k_5)\}}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}} \tag{16}$$

finally becoming independent at a high halide concentration (Eq. 17). The activity of the halide may be measured by the value of k_5 (Reaction 13e). At low halide concentration, when $k_5[\mathrm{H}]$ is small,

$$J = \frac{k_1[\mathrm{Os_3(CO)_{12}}][\mathrm{M}]I_0\{[\mathrm{H}] + (k_6'/k_5)\}}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}} \tag{17}$$

At high [halide], when $k_5[\mathrm{H}]$ is large,

$$J = \frac{k_1[\mathrm{OS_3(CO)_{12}}][\mathrm{M}]I_0}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}} \tag{18}$$

Equations (14) and (15) are consistent with our observations. The curve calculated from Eq. (14) and presented in Fig. 2 agrees satisfactorily with the experimental points.

The increase of the quantum yield of initiation occurs with the increase of [halide] and finally reaches a plateau value. Our observation is consistent with Eq. (19), and the curve calculated from the equation is shown in Fig. 7.

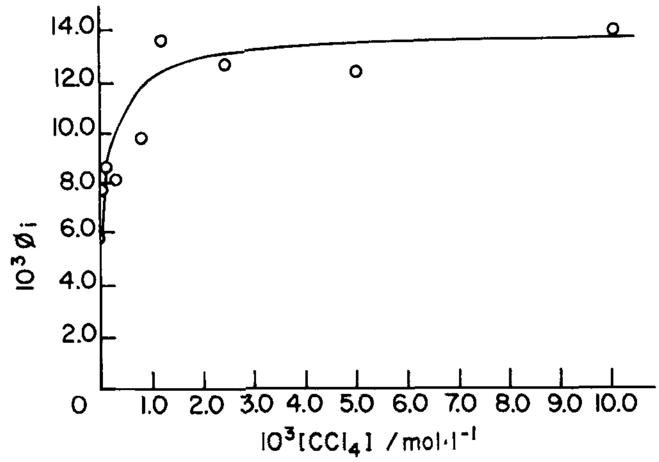

FIG. 7. Dependence of quantum yields of initiation on [CCl$_4$]. Curve calculated from Eq. (19) by using kinetic parameters presented in Table 9.

$$\phi_i = \frac{\{[\mathrm{H}] + (k_6'/k_5)\}}{\{[\mathrm{M}] + (k_2/k_3)\}\{1 + (k_d/k_4)\}\{[\mathrm{H}] + (k_7'/k_5) + (k_6'/k_5)\}} \tag{19}$$

and at high [CCl$_4$], ϕ_i is given by

$$\phi_i = \frac{1}{\{1 + (k_2/k_3[\mathrm{M}])\}\{1 + (k_d/k_4)\}} \tag{20}$$

Further, at high [CCl$_4$], Eq. (20) predicts an increase of quantum yield with an increase of monomer concentration because k_2/k_3[M] reduces with an increase of [M]. This is in agreement with our findings. It can be seen in Table 6 that the quantum yield of initiation is very low ($\phi_i \approx 0.013$) at high [CCl$_4$]. The low ϕ_i indicates the necessity of postulating a backreaction as put forward in Reaction (13a) and $k_2 >> k_3$[M]. The ratio of the rate constants were evaluated from Eq. (13) by assuming a steady-state concentration of the intermediates. Thus, we can write:

$$[\mathrm{Os}^*] = \frac{k_1 h\nu[\mathrm{Os}]}{k_2 + k_3[\mathrm{M}]}$$

where [Os] = [Os$_3$(CO)$_{12}$].

$$[\mathrm{I}] = \frac{k_3[\mathrm{M}]k_1 h\nu[\mathrm{Os}]}{(k_d + k_4)(k_2 + k_3[\mathrm{M}])}$$

and

$$[\mathrm{II}] = \frac{k_1 k_4 k_3[\mathrm{M}][\mathrm{Os}]h\nu}{(k_5[\mathrm{H}] + k_6' + k_7')(k_d + k_4)(k_2 + k_3[\mathrm{M}])}$$

then

$$J = k_6'[\mathrm{II}] + k_5[\mathrm{H}][\mathrm{II}]$$

$$= \frac{(k_6' + k_5[\mathrm{H}])(k_1 k_3[\mathrm{M}]k_4[\mathrm{Os}]h\nu)}{(k_5[\mathrm{H}] + k_6' + k_7')(k_d + k_4)(k_2 + k_3[\mathrm{M}])}$$

At high [halide], when $k_6' = 0$

$$J = \frac{k_4 k_3[\mathrm{M}][\mathrm{Os}^*]k_5[\mathrm{H}]}{(k_5[\mathrm{H}] + k_7')(k_d + k_4)}$$

$$\frac{1}{J} = \frac{\{1 + (k_d/k_4)\}}{k_3[\mathrm{M}][\mathrm{Os}^*]} + \frac{k_7'\{1 + (k_d/k_4)\}}{k_3[\mathrm{M}][\mathrm{Os}^*]k_5[\mathrm{H}]}$$

A plot of $1/J$ as a function of $1/[\mathrm{H}]$ provides an intercept of 0.20×10^9 and a slope of 3×10^4. Thus,

$$\text{Intercept} = \left(1 + \frac{k_d}{k_4}\right)\frac{1}{k_3[\mathrm{M}][\mathrm{Os}^*]} \tag{21}$$

$$\text{Slope} = \left(1 + \frac{k_d}{k_4}\right)\frac{1}{k_3[\mathrm{M}][\mathrm{Os}^*]}\,\frac{k_7'}{k_5} \tag{22}$$

Since $k_3[\mathrm{M}][\mathrm{Os}^*]$ = maximum rate of initiation, by substituting the value of $k_3[\mathrm{M}][\mathrm{Os}^*]$ in Eq. (21) we get $k_d/k_4 = 0.1$. The ratio of the rate constants k_7'/k_5 can be obtained from Eqs. (21) and (22), and $k_7'/k_5 = 1.5 \times 10^{-4}$.

TABLE 9. Kinetic Parameters Evaluated from Eq. (14) for the Photopolymerization of MMA at 25°C, λ = 365 nm

k_d/k_4	k_2/k_3, mol/L	k_6'/k_5, mol/L	k_7'/k_5, mol/L
0.1	6.10×10^2	10^{-4}	1.5×10^{-4}

Determination of the Kinetic Parameter k_2/k_3

At high [halide],

$$J = \frac{(k_3k_4[\mathrm{M}]k_1[\mathrm{Os}]h\nu)/(k_d + k_4)}{k_2 + k_3[\mathrm{M}]} \tag{23}$$

$$\frac{J}{I_{\mathrm{abs}}} = \frac{k_3k_4[\mathrm{M}]}{(k_2 + k_3[\mathrm{M}])(k_d + k_4)}$$

Since $J/I_{\mathrm{abs}} = \phi_i$, and at high [halide] $\phi_i = 0.01$, $k_d/k_4 = 0.1$, and [M] = 9.38 mol/L, by substituting these values in Eq. (23) we get $k_2/k_3 = 610$.

Determination of the Kinetic Parameter k_7'/k_6'

When [halide] = 0, J is given by

$$J = \frac{k_1k_3k_4k_6'[\mathrm{M}][\mathrm{Os}]h\nu}{(k_6' + k_7')(k_d + k_4)(k_2 + k_3[\mathrm{M}])} \tag{24}$$

By rearranging Eq. (24), we get

$$J = \frac{I_{\mathrm{abs}}}{\{1 + (k_7'/k_6')\}\{1 + (k_2/k_3[\mathrm{M}])\}\{1 + (k_d/k_4)\}} \tag{25}$$

By substituting the values of k_d/k_4, k_2/k_3, I_{abs}, [M], and J at $\mathrm{CCl_4} = 0$ in Eq. (25), $k_7'/'_6$ is evaluated and $k_7'/k_6' = 1.33$. The value of the remaining ratio of the rate constants k_6'/k_5 is obtained from k_7'/k_6' and k_7'/k_5, and k_6'/k_5 is found to be 10^{-4}.

The ratio of the rate constants are presented in Table 9. The theoretical curves calculated by using these kinetic parameters agreed well with the observations (Figs. 2 and 7). These findings strongly suggest that the proposed mechanism is correct. The mechanism of the initiation reaction in the presence of halide with $Os_3(CO)_{12}$ is similar to that of other carbonyls so far studied. The peculiarities observed in this system are its low quantum yield of initiation and its capability to initiate polymerization by hydrogen abstraction in the absence of organic halide. The rate of polymerization is also significantly influenced by the type of monomer chosen for polymerization.

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REFERENCES

[1] C. H. Bamford, J. Hobbs, and R. P. Wayne, *Chem. Commun.*, p. 469 (1965).

[2] C. H. Bamford, P. A. Crowe, and R. P. Wayne, *Proc. R. Soc., A, 284*, 455 (1965).

[3] C. H. Bamford, in *New Trends in the Photochemistry of Polymers* (N. S. Allen and J. F. Rabek, eds.), Elsevier, New York, 1985, p. 129.

[4] C. H. Bamford, P. A. Crowe, J. Hobbs, and R. P. Wayne, *Proc. R. Soc., A, 292*, 153 (1966).

[5] W. Strohmeier and H. Grubel, *Z. Naturforsch, 22B*, 115 (1967).

[6] C. H. Bamford, G. C. Eastmond, and D. Whittle, *Polymer, 10*, 771 (1969).

[7] C. H. Bamford and M. U. Mahmud, *Chem. Commun.*, p. 762, (1972).

[8] C. H. Bamford, *Pure Appl. Chem., 34*(2), 173 (1973).

[9] J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci., 12*, 449 (1954).

[10] M. S. Matheson, E. E. Auer, E. E. Bevilacqua, and E. S. Hart, *J. Am. Chem. Soc., 71*, 495 (1949).

[11] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc., A*, p. 2859 (1968).
[12] A. M. North and G. A. Reed, *Trans. Faraday Soc., 57*, 859 (1961).
[13] C. G. Hatchard and C. A. Parker, *Proc. R. Soc., A, 235*, 518 (1956).

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