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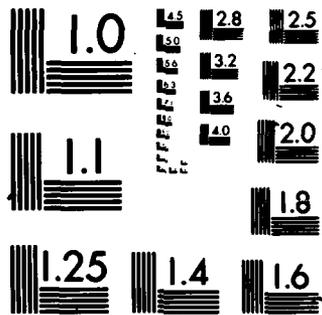
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Reaction Kinetics of the Intermediate Produced in the
Laser Pulse Photolysis of Tungsten Hexacarbonyl in Fluid Solution.

by

Alistair J. Lees and Arthur W. Adamson

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Los Angeles, California 90007

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**Reaction Kinetics of the Intermediate Produced in the
Laser Pulse Photolysis of Tungsten Hexacarbonyl in Fluid Solution.**

Alistair J. Lees and Arthur W. Adamson

Department of Chemistry, University of Southern California, Los Angeles,
California 90007.

$\epsilon_{\text{max}} = 7,500 \text{ M}^{-1} \text{ cm}^{-1}$

Abstract

$1,900,000 \text{ S}^{-1}$ to the -1 power

$k_{\text{sub}2} / k_{\text{sub}1} \text{ appx. } 270$

Laser pulse photolysis at 353 nm of tungsten hexacarbonyl in room temperature methylcyclohexane produces an intermediate, proposed to be $\text{W}(\text{CO})_5\text{S}$, S denoting solvent, with an absorption maximum at 425 nm and $\epsilon_{\text{max}} = 7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. In the presence of added L = 4-acetylpyridine, the intermediate reacts completely to form $\text{W}(\text{CO})_5\text{L}$ as final product. The rate of disappearance of the intermediate is pseudo first order, with $k_{\text{app}}^{\text{I}}$ linear in (L) at low concentration but approaching a limiting value at higher concentrations. The proposed mechanism is one of reversible dissociation of $\text{W}(\text{CO})_5\text{S}$ to $\text{W}(\text{CO})_5^{\text{I}}$ and S with rate constants $k_{\text{sub}1}$ and $k_{\text{sub}2}$, followed by scavenging of the $\text{W}(\text{CO})_5^{\text{I}}$ by L, with rate constant $k_{\text{sub}3}$. At 20 °C $k_{\text{sub}1} = 1.9 \times 10^6 \text{ s}^{-1}$ and $k_{\text{sub}2} / k_{\text{sub}1} = 270$, the corresponding activation quantities are $E_1 = 3.9 \text{ kcal mole}^{-1}$ and $(E_2 - E_1) = 2.6 \text{ kcal mole}^{-1}$. The nature of the primary photolysis step is discussed.

$k_{\text{sub}1}$

$k_{\text{sub}1}$

$k_{\text{sub}2}$

$E_{\text{sub}1}$

$E_{\text{sub}2}$

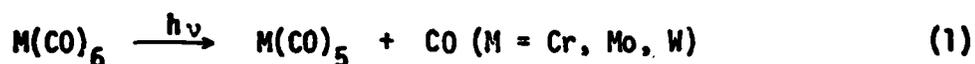
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Introduction

The photochemical behavior of organometallic complexes is of importance to the production of catalytically active compounds and to the advancement of synthetic organometallic chemistry.¹ In particular, intermediates produced in the photolysis of group VI hexacarbonyls have been the subject of an increasing number of investigations. The primary photoreaction appears to be one of efficient CO dissociation:²⁻⁴



In the presence of coordinating ligand L the substitution product $\text{M}(\text{CO})_5\text{L}$ is formed with near unitary quantum efficiency.² It is the structure, the solvation, and the reaction kinetics of the $\text{M}(\text{CO})_5$ species that has been of much interest.

In a classical study, Stolž, Dobson and Sheline^{5,6} found the infrared absorption spectrum of $\text{M}(\text{CO})_5$ produced in iso-pentane/methylcyclohexane glasses at 77K to be consistent with a C_{4v} square pyramidal structure, but with isomerization to a D_{3h} trigonal bipyramidal structure on thawing of the glass. Extensive investigations by Turner and co-workers⁷⁻⁹ further supported the presence of a C_{4v} intermediate in low temperature matrices, and one able to undergo thermal reaction with the photoproduced or added CO. A suggestion¹⁰ that $\text{M}(\text{CO})_5$ could be weakly coordinating to even poor donors was substantiated by evidence for $\text{M}(\text{CO})_5\text{N}_2$ in N_2 or Ar/N_2 matrices at 20 K,⁸ and, more specifically, for weak bonding between $\text{Cr}(\text{CO})_5$ and rare gas or hydrocarbon in the corresponding matrices.^{9,11}

$\text{M}(\text{CO})_5$ intermediates have also been examined in room temperature fluid solution by means of conventional flash photolysis and pulse radiolysis techniques.¹²⁻¹⁷ Kelly et al¹⁴ reported that on flash

photolysis of $\text{Cr}(\text{CO})_6$ in cyclohexane, an intermediate was produced with an absorption maximum at 503 nm, thought to be $\text{Cr}(\text{CO})_5$ and highly reactive toward solvent impurities. However, more recent work suggests that the intermediate may have been $\text{Cr}(\text{CO})_5\text{S}$, S denoting solvent. The intermediate produced in perfluorocarbon solvents was found to combine with CO , N_2 , and cyclohexane with rate constants at about the diffusion limit,¹⁶ so that in cyclohexane as solvent the immediately produced species should be the solvent coordinated one. There is thus some gathering of evidence that the first observed intermediate both in fluid solution and in low temperature matrices is not $\text{M}(\text{CO})_5$ but $\text{M}(\text{CO})_5\text{S}$, although the M-S bond may be a weak one.

We report in this paper the observation of an intermediate following photolysis of $\text{W}(\text{CO})_6$ in methylcyclohexane solvent at room temperature, and on the kinetics of its subsequent reaction with 4-acetylpyridine. The experiment is one of monitoring absorbance changes, following pulsed laser photolyses.

Experimental

Materials. - Tungsten hexacarbonyl (Strem Chemicals) was purified by sublimation. The ligand 4-acetylpyridine (Aldrich) was used without further purification. Solvents used were obtained from MCB Manufacturing Chemists and were OmniSolv grade. The methylcyclohexane, however, was further purified by several distillations, so as to remove emitting impurities.

$\text{W}(\text{CO})_5(4\text{-acetylpyridine})$. - The compound was prepared by reacting photogenerated $\text{W}(\text{CO})_5(\text{tetrahydrofuran})$ with 4-acetylpyridine, according to a literature procedure,^{4,18} in tetrahydrofuran (THF) solvent. The THF was removed by rotary evaporation and the solid product was dissolved

in iso-octane and purified by chromatography on alumina (MCB Manufacturing Chemists). Elution was first with iso-octane until the uv absorption features of $W(CO)_6$ could no longer be detected in the eluant, followed by elution of the product complex with benzene. The product was recovered by rotary evaporation. The infrared and uv-visible absorption spectra agreed well with those published.¹⁸ Chemical analysis gave: C, 32.9%; H, 1.8%; N, 3.3%. The corresponding calculated values are 32.4%, 1.6%, and 3.1%.

Equipment and procedures. - Details of the laser photolysis and monitoring equipment are described elsewhere.^{19,20} Excitation was at 353 nm, using 20 nsec, frequency tripled pulses from the Nd glass laser. The pulse energy was measured by means of the photodiode pulse produced by a portion of the beam and recorded as one of the oscilloscope traces, so that correction could be made for the $\pm 10\%$ variation in laser pulse energy. Absolute pulse energies were checked by means of a Korad model 108 ballistic thermopile, and were in the 90-140 mJ range, depending on the laser power settings. The one cm diameter laser beam was shaped by means of a cylindrical lens to give an irradiated area of 2x9 mm on the front window of a four clear-sided quartz cell. The temperature of the solution in the cell was controlled to 0.1 °C by circulating thermostatted water.

The transmitted monitoring beam was reduced down onto the slit of a Jarrell-Ash Mark 10 monochromator, and exited onto a five-stage RCA 4840 photomultiplier. Typical entrance and exit slits were 1 mm. Saturation effects were avoided by employing a mechanical shutter.²⁰ Solutions were deaerated by argon purging for twenty minutes, as a precautionary measure although lack of such purging had no measurable effect. Conventional absorption spectra were obtained by means of a Cary 14R recording spectrophotometer.

Results

A typical experiment consisted of excitation of a methylcyclohexane solution which was 5×10^{-5} M in $W(CO)_6$ and around 0.02 M in 4-acetylpyridine. The transmitted intensity of the monitoring beam showed an instantaneous decrease from V_0 to V_{in} , that is, a decrease which followed the 20 nsec laser pulse half-time. A measurably slow further change then occurred, in which V_t , the intensity at time t after the pulse, dropped to a final value V_{∞} . Here, V denotes voltage of the oscilloscope signal from the photomultiplier. Since $W(CO)_6$ does not absorb in the 400-600 nm region, $\log(V_0/V_{\infty})$ gives the optical density of the final product, D_{∞} and is thus proportional to its extinction coefficient. The variation of D_{∞} with wavelength corresponded closely to the absorption spectrum of $W(CO)_5$ (4-acetylpyridine), with maxima at 404 nm and 442 nm. This is shown in Fig. 1, with the D_{∞} values scaled to be the known molar extinction coefficients. The actual degree of photolysis by a single laser pulse was about 50%, that is, the observed D_{∞} 's were about half of those calculated for complete reaction.

Next, $\log(V_{\infty}/V_{in})$ gave $D_{in} - D_{\infty}$, the difference in optical densities of unreacted transient and final product, so that D_{in} values could be calculated. This intermediate will be identified as a pentacarbonyl, and almost certainly was fully converted to final product in view of the great excess of 4-acetylpyridine over the small amount of competitor CO produced in the photolysis. On this basis, D_{in}/D_{∞} is also the ratio of the respective extinction coefficients, and it was thus possible to obtain absolute molar extinction coefficient values for the transient. The plot of these is included in Fig. 1. The value of ϵ_{max} is $7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 425 nm, and the position of the maximum is within the range of wavelengths reported for tungsten pentacarbonyl species generated in low temperature

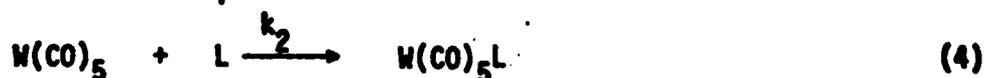
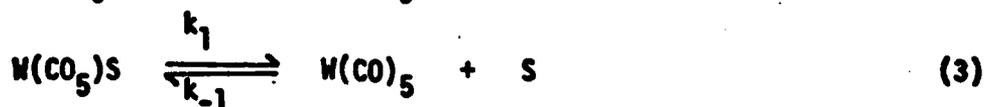
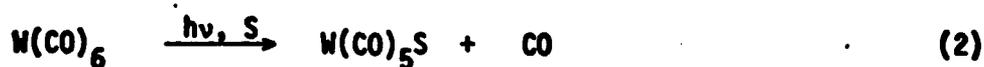
matrices, SF₆ (461 nm), Ar (437 nm), Xe (417 nm), and CH₄ (413 nm),⁹ as well as in the pulsed radiolysis study in cyclohexane (415 nm).¹⁷ The same transient absorption spectrum as reported here is found on pulse photolysis of W(CO)₅L complexes in methylcyclohexane, with L = 4-cyanopyridine, 4-acetylpyridine, and 4-benzoylpyridine.²¹

The growth D_{in} to D_∞ was exponential, that is, ln (D_t - D_∞) varied linearly with time over the full run of the oscilloscope traces. Data were usually taken at 480 nm, but it was checked that the k_{app} values obtained from the slope of such plots did not vary with monitoring wavelength over the range 400-500 nm. These k_{app} values were linear in 4-acetylpyridine concentration (L) at low concentrations, but showed saturation at higher ones, as illustrated in Fig. 2.

Photoexcited emission from W(CO)₆ may have been marginally present but, if so, it followed the laser pulse. In contrast, then, to the above W(CO)₅L complexes,²² emitting species, if present, were less than 5 nsec in lifetime (for these experiments, the laser pulse was gated down to 5 nsec half-time).

Discussion

The simplest explanation of our kinetic results appears to be the following. We take the first observable product, our transient, to be W(CO)₅S, and write the sequence:



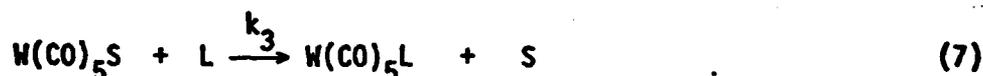
Steady state analysis gives:

$$d[W(CO)_5S]/dt = k_{app} [W(CO)_5S] \quad (5)$$

$$k_{app} = \frac{k_2 k_1 (L)}{1 + k_2 (L)/k'_{-1}} ; k'_{-1} = k_{-1}(S), K_1 = k_1/k_{-1} \quad (6)$$

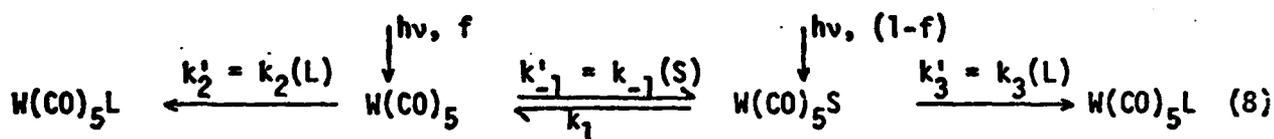
According to Eq. (6), a plot of $(L)/k_{app}$ vs. (L) should be linear with intercept $k'_{-1}/k_1 k_2$ and slope $1/k_1$. This behavior was indeed followed, as shown in Fig. 3, for several temperatures.

Before proceeding further, alternative mechanisms should be considered. First, direct bimolecular reaction between L and $W(CO)_5S$,



can be ruled out; $k_{app} = k_3$ does not saturate in this mechanism.

Another possibility is that $W(CO)_5$ is the initial transient species, with ensuing reaction either with L, or reversibly with S. The complete kinetic picture becomes that of Eq. (8).



In this general case, D_{in} might correspond to fraction f of $W(CO)_5$ and $(1-f)$ of $W(CO)_5S$. The solution for this set of coupled reactions is known, see Refs. 26 and 27, and it was possible to search for a set of rate constant and f values that would fit our observations. The general solution contains two exponentials, $e^{-\lambda_1 t}$ and $e^{-\lambda_2 t}$, where $\lambda_{1,2}$ are solutions to a quadratic equation in the rate constants; the rate law is thus biphasic in the appearance of $W(CO)_5L$. One constraint is that the relative rate constant values be such that $\lambda_1 > \lambda_2$ so that we could observe single exponential behavior in our time regime. Another is that the

resulting k_{app} show saturation with increasing (L). Briefly, no suitable regime of rate constants would be found to satisfy both constraints except for the limiting case of $f = 0$, $k_3 = 0$, corresponding to Eqs. (2)-(4), and then only if $k'_{-1} > k_1$.

We can therefore return to the proposed mechanism. It indeed seems physically reasonable that $W(CO)_5S$ be the intermediate; that is, our transient species. The various matrix isolation experiments show the absorption spectrum to be medium dependent, so solvent is in some manner implicated. Eq. (6) now gives meaning to the slopes and intercepts of Fig. 3. At 20 °C we find $k_1 = 1.9 \times 10^6 \text{ s}^{-1}$ and $k_2/k'_{-1} = 34 \text{ M}^{-1}$. On correcting for solvent concentration, the preference ratio k_2/k'_{-1} becomes about 270, a number corresponding to an activation energy difference between reactions (3) and (4) of $3.3 \text{ kcal mole}^{-1}$.

The temperature dependence data of Fig. 3 yield good Arrhenius plots, from which we find $E_1^* = 3.9 \text{ kcal mole}^{-1}$ (whence $\Delta S_1^{\ddagger} = -16.5 \text{ cal K}^{-1} \text{ mole}^{-1}$) and $(E_{-1}^* - E_2^*) = 2.6 \text{ kcal mole}^{-1}$, the subscripts denoting the corresponding rate constants; the least squares uncertainty in the above values is about 1 kcal mole^{-1} . The relevant energy diagram is shown in Fig. 4, where the range $2.6 - 3.3 \text{ kcal mole}^{-1}$ for $(E_{-1}^* - E_2^*)$ includes the estimate from the value of the scavenging ratio. An average of $3.0 \text{ kcal mole}^{-1}$ would lie within both experimental error limits. We now, of course, have a kinetic estimate of the W-S bond energy as $3.9 \text{ kcal mole}^{-1}$, and can expect the W-L bond energy to be at least $3.9 + 3$ or about 7 kcal mole^{-1} .

We turn finally to the detailed nature of the primary photostep (2). This could consist of reaction (1) followed by rapid solvent coordination, but, if so, the $M(CO)_5$ species of reaction (1) cannot be the same as that of reaction (3), in view of the analysis around Eq. (8). A defensible possibility is that the former species is C_{4v} while the latter one is D_{3h} . Alternatively and perhaps indistinguishably, reaction (1) could be concerted. Yet another possibility, suggested by ligand field analysis of the d^6 case by Vanquickenborne and Ceulemans²⁸ (see also Ref. 29) is that the immediate product of reaction (1) is an excited state C_{4v} species, which relaxes to ground state C_{4v} and coordinates solvent. Our intermediate of reaction (3) would again be the D_{3h} species. The lifetime of an excited state C_{4v} complex must be short, however, since we see no indication of its presence either in emission or in transient absorption.

Acknowledgement

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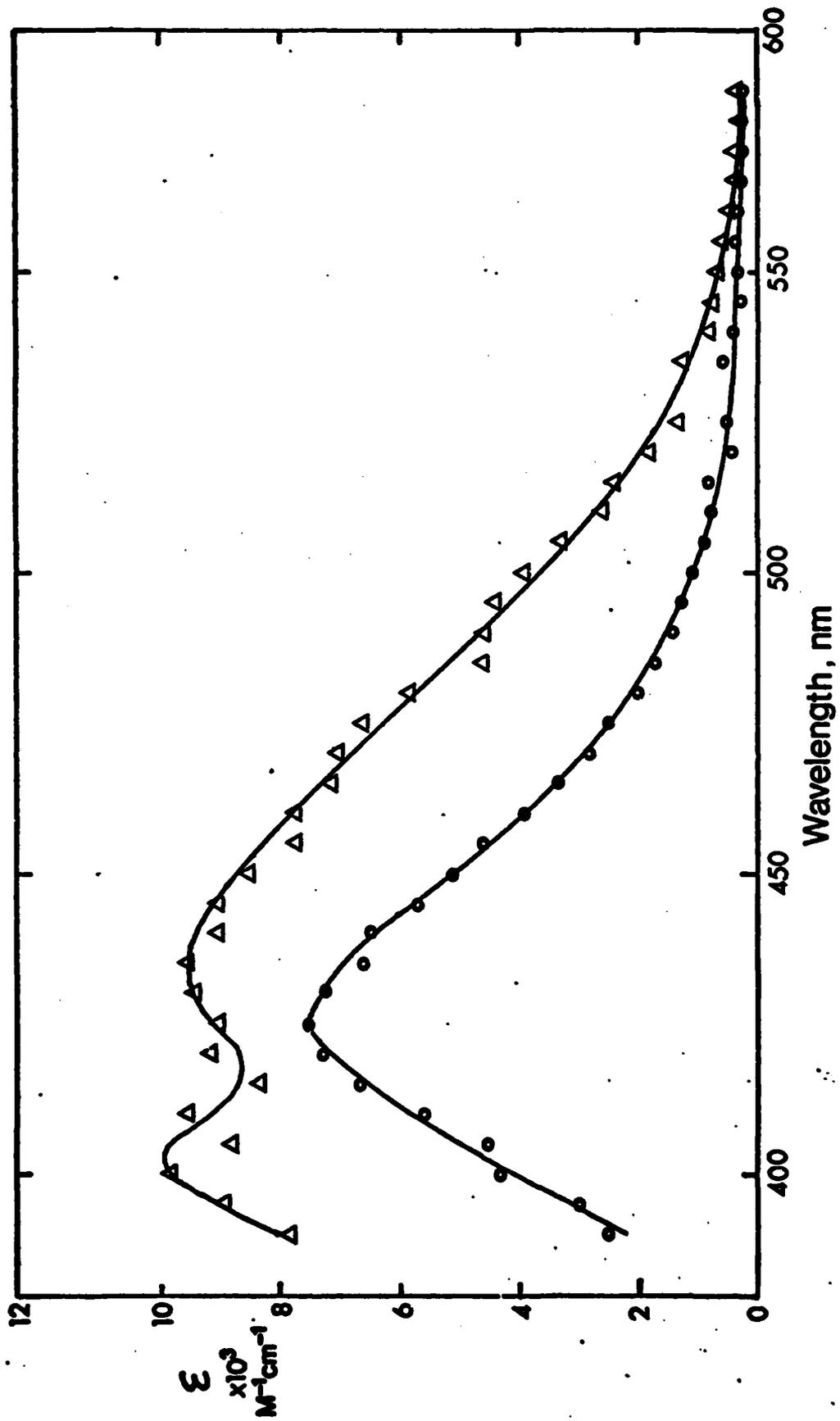
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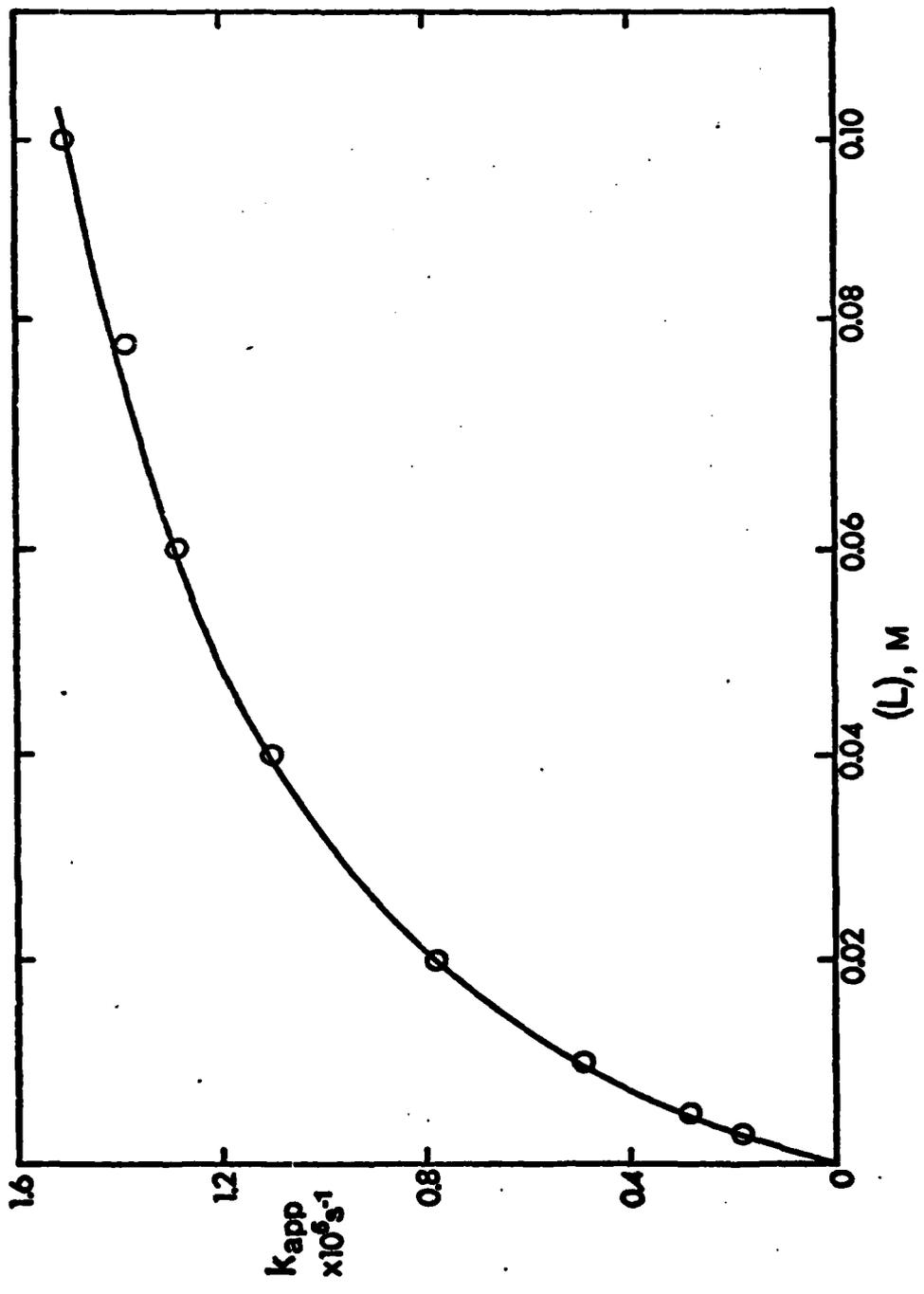
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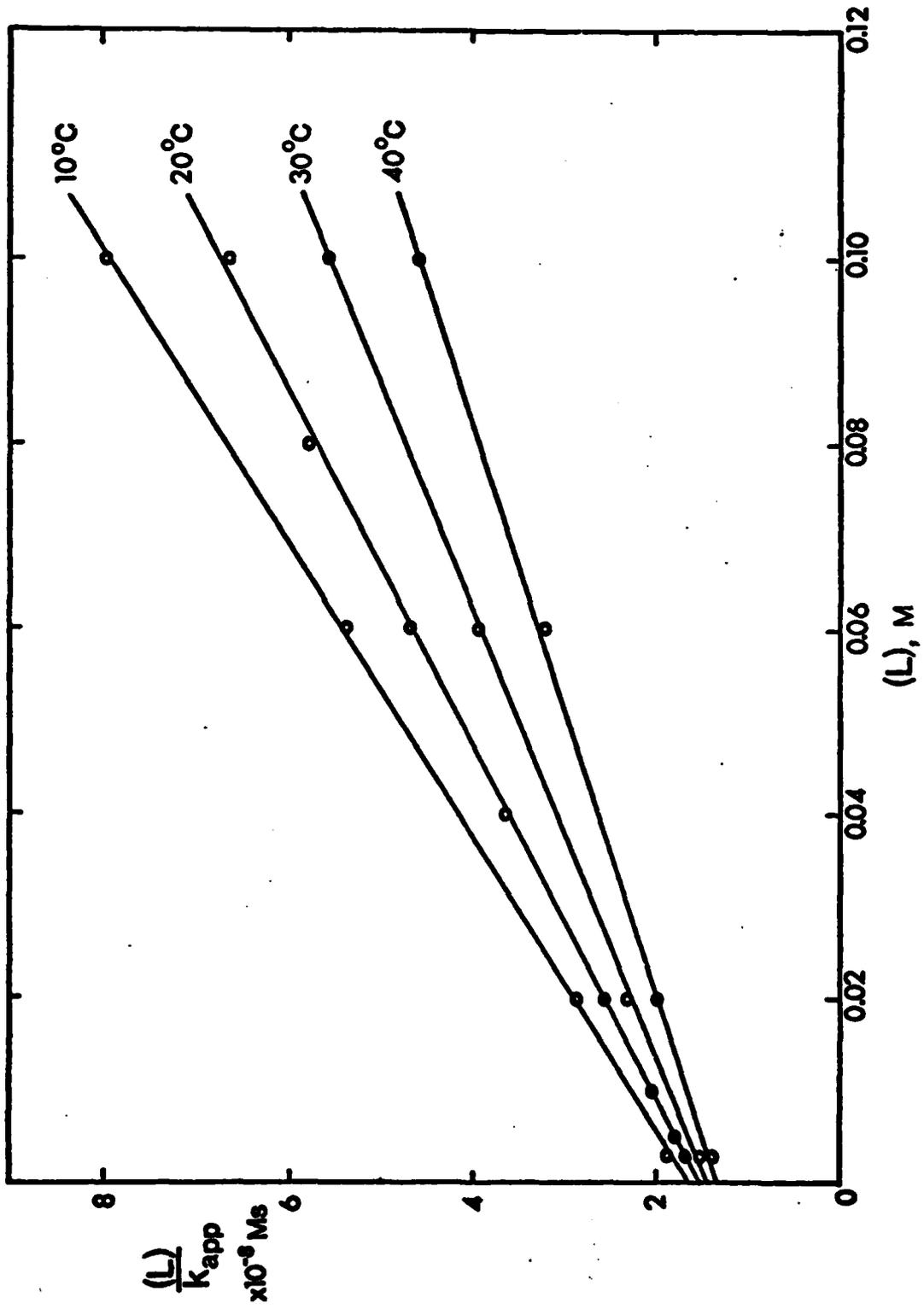
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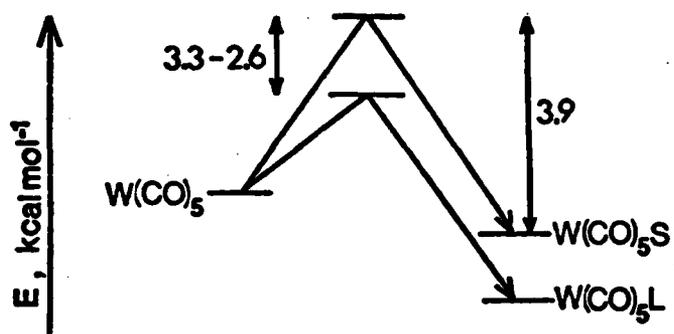
FIGURE LEGENDS

- Fig. 1. Absorption spectra recorded following laser pulse photolysis of $5 \times 10^{-4} \text{ M W(CO)}_6$ and $5 \times 10^{-3} \text{ M 4-acetylpyridine}$ in methylcyclohexane at 20°C ; \circ transient absorption spectrum recorded immediately following laser pulse. Δ Product absorption spectrum recorded after decay of transient.
- Fig. 2. The dependence of the observed first order rate constant, k_{app} in s^{-1} , for decay of the intermediate species on concentration of 4-acetylpyridine in a $5 \times 10^{-4} \text{ M W(CO)}_6$ methylcyclohexane solution.
- Fig. 3. Least squares lines of $\frac{(L)}{k_{\text{app}}}$ versus (L) at 10, 20, 30 and 40°C . (L) is the concentration of 4-acetylpyridine, in a $5 \times 10^{-4} \text{ M W(CO)}_6$ methylcyclohexane solution and k_{app} is the observed rate constant in s^{-1} , for decay of the intermediate species.
- Fig. 4. Energy diagram for $\text{W(CO)}_5\text{L}$, $\text{W(CO)}_5\text{S}$, and W(CO)_5 .









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