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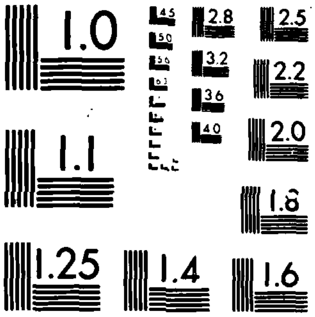

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A program involving the investigation and characterization of reactions of coordinatively unsaturated organometallic species is described. The program emphasizes the measurement of rates of reaction of photolytically produced coordinatively unsaturated species with the parent and rates for cluster formation. Experimental measurements are performed using a time resolved transient absorption apparatus which uses a line tunable CO laser to record spectral and kinetic information by means of probing absorptions in the CO stretch region of the infrared. Systems that have been investigated include coordinatively unsaturated species generated from the $Fe(CO)_5$, $Cr(CO)_6$ and $Mn_2(CO)_{10}$ parents. The results of experiments with these systems are briefly discussed.

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The Spectroscopy and Reaction Kinetics of Coordinated Unsaturated Metal Carbonyls

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Coordinatively unsaturated metals are important chemical species with a variety of interesting and unique chemical properties. These species have been shown to be exceedingly reactive. They are important catalysts, reaction intermediates and can form oligomers and metal clusters containing multiple metal centers.[1] Despite their importance and a great deal of interest in this area, little is known regarding details of the structure or reactivity of coordinatively unsaturated metals. Their extreme reactivity has heretofore been an impediment to detailed study of these species in the liquid phase and has virtually precluded study in the gas phase. Until recently nothing was known about the mechanism or kinetics for reactions or cluster formation in these systems.

In an effort to alter that situation we have developed an apparatus and a technique which allows us to study coordinatively unsaturated metals in either phase in real time. The use of transient absorption spectroscopy has allowed us to detect and monitor coordinatively unsaturated metals. Briefly, the coordinatively unsaturated metals are generated via excimer laser photolysis of appropriate precursors. Most of our work to date has involved volatile metal carbonyls which are photolyzed to yield gas phase coordinatively unsaturated metal carbonyls or metal atoms. Most of our work has employed an apparatus that uses a line tunable CO laser, as a probe, to monitor the change in absorption of the sample following the excimer laser photolysis pulse. However, we have now integrated a cw diode laser into the apparatus. This allows us to probe transient species in any region of the infrared and thus vastly increase the versatility of the apparatus.

To actually generate a transient spectrum the change in absorption of the probe laser is monitored at a variety of different laser frequencies with the time versus absorbance signal digitized via a transient digitizer which feeds the data to a signal averager from which it is fed to a computer. The computer takes all the frequency dependent data and assembles it into a transient absorption spectrum which can be displayed as a function of time following the photolysis pulse. Once features in the transient absorption spectrum are identified, a specific feature can be monitored as a function of time and its kinetic behavior discerned. Our current apparatus has a time response of 30 nsec, a frequency range of 350-2350 and 2900-3300 cm^{-1}, and a typical detection sensitivity corresponding to 10^9 coordinatively unsaturated metal carbonyl molecules.

With the above technique, we have been able to obtain the first gas phase infrared spectrum of a coordinatively unsaturated metal.[2] We have obtained infrared spectra in the CO stretch region for the species $Fe(CO)_x$ ($x = 2,3,4$) and have measured the rate of reaction of $Fe(CO)_x$ with CO and the activation energies for these reactions.[3] We have made the first real time observation of and are measuring the kinetics for clustering of $Fe(CO)_x$ species.[4] We are also investigating the inhibition of clustering on addition of other ligands to the system. We have performed similar studies for the $Cr(CO)_6$ system, looking at spectra for $Cr(CO)_x$ ($x = 2,3,4,5$)[5] and have measured rates of reactions of $Cr(CO)_5$ with CO, CH_4, N_2, H_2 and C_6H_6.[6] We have also observed a heretofore unreported clustering process in the $Cr(CO)_x$ system. We find that all the $Cr(CO)_x$ fragments react readily with parent. In particular, we have investigated in detail the clustering process for the reaction of $Cr(CO)_4$ and $Cr(CO)_5$ with parent. We find that both reactions occur at a rate that is within a factor of two of gas kinetics. We assign the species initially produced via these clustering reactions to $Cr_2(CO)_{10}$ and $Cr_2(CO)_{11}$, respectively, and have recorded the first gas phase spectra for these species in the carbonyl stretch region.[6]

We have also obtained results on the $Mn_2(CO)_{10}$ system.[7,8] As with $Cr(CO)_6$ and $Fe(CO)_5$, we have recorded the spectra of the photofragments identified following photolysis at 193, 249 and 351 cm^{-1}.[8] We have identified the major photoproducts and have measured the rate of reaction of $Mn_2(CO)_9$ with CO and the rate of reaction of two $Mn(CO)_5$ radicals to regenerate $Mn_2(CO)_{10}$. Interestingly, the reaction of $Mn_2(CO)_5$ with CO is quite slow and we are exploring the structural ramifications of this observation. The reaction of $2Mn(CO)_5$ radicals is very rapid, almost gas kinetic, and represents the first measurement of the actual rate of formation of a metal-metal band in the gas phase.

The above work has allowed us to produce a hypothesis regarding the mechanism of photodissociation in these systems and allows us to have some insight into how to tailor the dissociation process to produce desired photoproducts. It also allows us to intelligently speculate on the timescale for liquid dissociation.

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8. T. A. Seder, S. P. Church and E. Weitz, submitted to J. Am. Chem. Soc.

Publications Supported Under This Contract

a) Gas Phase Photofragmentation of $Cr(CO)_6$: Time Resolved Infrared Spectrum and Decay Kinetics of "Naked" $Cr(CO)_5$. T. A. Seder, Stephen P. Church, A. J. Ouderkirk and Eric Weitz. J. Am. Chem. Soc. 107, 1432 (1985). ✓

b) The Generation and Detection of Coordinatively Unsaturated Organometallic Species. Martyn Poliakoff and Eric Weitz, to be published in Annual Review of Organometallic Chemistry, 1985.

c) Gas Phase Infrared Spectroscopy and Recombination Kinetics for $Mn(CO)_5$ Generated via XeF Laser Photolysis of $Mn_2(CO)_{10}$. T. A. Seder, S. P. Church and Eric Weitz. Submitted to J. Am. Chem. Soc. ✓

d) The Spectroscopy and Reaction Kinetics of Photolytically Generated Coordinatively Unsaturated Organometallics in the Gas Phase: $Fe(CO)_x$ ($x = 2,3,4$). T. A. Seder, A. J. Ouderkirk and Eric Weitz. Manuscript in preparation - to be published in J. Am. Chem. Soc. ✓

e) The Spectroscopy and Reaction Kinetics of Photolytically Generated Coordinatively Unsaturated Organometallics in the Gas Phase: $Cr(CO)_x$ ($x = 2,3,4,5$). T. A. Seder, S. P. Church and Eric Weitz. Manuscript in preparation, to be published in J. Am. Chem. Soc.

Associated personnel

T. A. Seder - graduate student
S. Gravelle - graduate student
S. P. Church - postdoctoral research associate

Papers presented relating to project area

Seminars:	Beloit College	10/84
	Columbia University	9/85

Meetings:	American Chemical Society - Pacific Basin Symposium on New Methods in Transient Spectroscopy	12/84
	American Chemical Society - National Meeting Chicago, IL. Symposium on Transient Species	9/85
	IUPAC Meeting - Manchester, England Symposium on New Methods in Infrared Spectroscopy	9/85
Workshops:	NSF sponsored workshop on Organometallic Photochemistry - Boulder, CO	6/85

Gas Phase Infrared Spectroscopy and Recombination Kinetics for $Mn(CO)_5$ Generated via XeF Laser Photolysis of $Mn_2(CO)_{10}$

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Abstract

Direct spectroscopic evidence is presented for the generation of $Mn(CO)_5$ upon XeF laser (351 nm) photolysis of gas phase $Mn_2(CO)_{10}$. The $Mn(CO)_5$ species is detected via its infrared absorptions in the carbonyl stretch region. By correlation with results of condensed phase experiments, the gas phase $Mn(CO)_5$ species is postulated to adopt a C_{4v} geometry. The gas phase species displays second order recombination kinetics. A rate constant for the recombination reaction of $(2.7 \pm 0.6) \times 10^{13}\ cm^3 \ell^{-1} sec^{-1}$ is reported. The nature of other photochemically generated fragments is discussed.

There is currently intense interest in the photochemistry of metal carbonyls, in part due to the important role played by highly reactive coordinatively unsaturated species in a variety of reaction mechanisms. There is also considerable interest in the structure and bonding of these species. Of particular interest are those species such as $Mn_2(CO)_{10}$ having a metal-metal bond. Because of this metal-metal bond two distinct types of primary photochemical events can occur; one involving loss of CO without metal-metal bond cleavage and the other involving homolytic cleavage of the Mn-Mn bond. Both processes have been reported in the uv photolysis of solution phase $Mn_2(CO)_{10}$,[1] and the relative yield of $Mn_2(CO)_9$ to $Mn(CO)_5$ has been noted to depend upon excitation wavelength.[2] $Mn_2(CO)_9$ has also been observed in a matrix environment.[3] In addition, the kinetics of the $Mn(CO)_5$ recombination reaction and the reaction of $Mn_2(CO)_9$ with CO have been measured in solution.[3]

Gas phase studies are considerably more limited. Freedman and Bersohn have measured the effect of polarized light on the angular distribution of fragments produced via photodissociation of $Mn_2(CO)_{10}$ setting an upper limit of several picoseconds on the excited state lifetime.[4] Leopold and Vaida's report of the presence of Mn_2 ion signals in the mass spectrum of the photoproducts generated via photolysis of gas phase $Mn_2(CO)_{10}$ suggests that CO loss is a photochemical pathway in the gas phase.[5]

In this Communication we report on the first example of direct detection via transient infrared spectroscopy of the $Mn(CO)_5$ radical produced via XeF (351 nm) laser photolysis of a gas phase sample of $Mn_2(CO)_{10}$. In addition the recombination kinetics of the $Mn(CO)_5$ radical have been studied, and a rate constant for recombination has been determined. Finally, we are able to make some comments on the nature of the primary photolytic processes occurring in $Mn_2(CO)_{10}$ for 351 nm radiation.

The time-resolved IR apparatus used for monitoring photochemically generated metal carbonyl transients in the gas phase has been previously described in detail.[6] Briefly, an excimer laser operating on XeF is used to photolyze $Mn_2(CO)_{10}$. Typically, 3 mj/cm^2 of laser radiation entered the photolysis cell. The output of a line-tunable liquid nitrogen-cooled CO laser is the IR probe. Changes in intensity of transmitted IR light were detected via a high speed InSb detector. The output of the detector was fed to appropriate amplifiers and subsequently signal averaged. Spectral data were obtained from transient absorption signals for each CO laser line of interest by having a computer join points corresponding to the amplitude of the transient signals at these frequencies for a given time delay following the photolysis pulse.

Kinetic data for $Mn(CO)_5$ recombination were obtained from transients at a given probe laser wavelength. In these experiments the source of $Mn_2(CO)_{10}$ was a small amount of solid placed on the bottom of the flow cell. This provided a pressure of ~2 mtorr of $Mn_2(CO)_{10}$ at room temperature. If desired, the cell could be warmed to 50°C to increase this pressure.

Figure 1 shows the IR spectrum obtained 25 μsec after photolysis of 2 mtorr of $Mn_2(CO)_{10}$ in the presence of 15 torr of Ar buffer at 21°C. Depletion (increase in transmitted intensity) of $Mn_2(CO)_{10}$ is evident at ~2023 cm^{-1} illustrating that net photolysis has occurred. The positive absorption (decrease in transmitted light intensity) at ~2000 cm^{-1} is assigned to the $Mn(CO)_5$ radical. The assignment is based on correlation with known absorptions of solution phase $Mn(CO)_5$ (1988 cm^{-1})[3] and the matrix isolated species (1987.6 cm^{-1} and 1978.4 cm^{-1}).[7] The observed difference in frequency between the gas phase and condensed phase bands for $Mn(CO)_5$ are compatible with the characteristic condensed phase red shifting of infrared absorption. 25 μsec is sufficient time for complete vibrational/rotational relaxation of the initially internally excited $Mn(CO)_5$ to have taken place. However, no significant reaction of $Mn(CO)_5$ has occurred on this timescale.

From studies involving the ^{13}CO substituted species, it has been shown that $Mn(CO)_5$ adopts the predicted[8] C_{4v} geometry in the matrix.[7] Thus the two bands observed in the matrix have been assigned to the E and A_1 vibrations, respectively. However, the E and A_1 bands were not resolved in solution[3] and, similarly, we have not, at present, been able to resolve these bands in the gas phase. Resolution of these bands is made more difficult by the convolution of the $Mn(CO)_5$ absorption with a parent band at 1993 cm^{-1}. This parent band, which is easily seen in the gas phase IR of $Mn_2(CO)_{10}$, is not observable as a negative feature in figure 1 due to an overlap with the intense $Mn(CO)_5$ absorptions. Our assignment implies that gas phase $Mn(CO)_5$ also is likely to have a C_{4v} geometry.

Identification of $Mn(CO)_5$ was confirmed by its kinetic behavior. Figure 2 shows a plot of the decay of the $Mn(CO)_5$ signal versus time. The decay clearly follows a second order rate law consistent with the reaction

$$2Mn(CO)_5 \xrightarrow{k_1} Mn_2(CO)_{10} \qquad (1)$$

Furthermore, as expected $Mn(CO)_5$ reacts rapidly with Cl_2 and is inert to CO on the timescale of our experiments. Also, $Mn_2(CO)_{10}$ is seen to be regenerated as $Mn(CO)_5$ is depleted. From the data in figure 2 a rate constant of

$\frac{(2.7 \pm 0.5) \times 10^{17}}{\varepsilon}$ $cm^5 mole^{-2} sec^{-1}$ can be determined for the rate of reaction of $Mn(CO)_5$, where ε is the absorption coefficient at the peak of the 2000 cm^{-1} band. If the peak absorption coefficient for the 2000 cm^{-1} band of $Mn(CO)_5$ is taken to be the same as peak absorption coefficient for the corresponding band in $Mn(CO)_5Cl$, $(10^7 cm^2 mol^{-1})$,[3] then the rate constant of equation 1 is $(2.7 \pm 0.5) \times 10^{13}$ $cm^3 mol^{-1} sec^{-1}$. This rate constant is quite close to that expected for a gas kinetic radical-radical recombination process, which is calculated to be $\sim 1 \times 10^{14}$ $cm^3 mol^{-1} sec^{-1}$. This result is consistent with liquid phase kinetic measurements, in which nearly diffusion controlled rates have been observed for reaction (1).[3]

Interestingly, all of the initially photolyzed $Mn_2(CO)_{10}$ is not regenerated via reaction of $Mn(CO)_5$. Moreover, though $Mn(CO)_5$ is inert to CO, addition of CO does lead to an increase in both the rate of regeneration and amount of $Mn_2(CO)_{10}$ regenerated. This is compatible with the regeneration of parent via reaction of CO with a photoproduct of $Mn_2(CO)_{10}$ which was produced via CO loss. By analogy with solution phase studies, the simplest of these species is $Mn_2(CO)_9$, though other species which have lost one or more COs are also possible. Thus we are presently working to verify whether $Mn_2(CO)_9$ can be detected via its characteristic semi-bridging CO absorption in the 1750 cm^{-1} region. We are also investigating the possible production of other photoproducts which have lost one or more COs, such as $Mn(CO)_x$ $(x < 5)$ and $Mn_2(CO)_y$ $(y < 9)$.

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Figure Captions

Figure 1. Transient infrared absorption spectrum obtained 25 μsec following XeF laser photolysis of gas phase $Mn_2(CO)_{10}$. The positive feature at 2000 cm^{-1} is attributed to a $Mn(CO)_5$ absorption. The negative features arise from photolytic depletion of $Mn_2(CO)_{10}$. Infrared absorptions of gas phase $Mn_2(CO)_{10}$ and CO matrix isolated $Mn(CO)_5$ are denoted by down arrows and up arrows, respectively. The tic marks above the ordinate depict the probe frequencies used to construct the spectrum.

Figure 2. Disappearance of $Mn(CO)_5$ presented as a second order decay. The data displayed in this figure were obtained from the transient absorption of $Mn(CO)_5$ at 2004.3 cm^{-1}. The transient waveform, which is shown over a 2 msec range (inset), was obtained under the conditions described in the text, except that the cell temperature was 50°C. From the slope of the curve, I/I_0 measurements, and an estimated extinction coefficient, the rate constant for the second order decay of $Mn(CO)_5$ is calculated to be $(2.7 \pm 0.6) \times 10^{13}$ $cm^3 mole^{-1} sec^{-1}$.

Figure 1

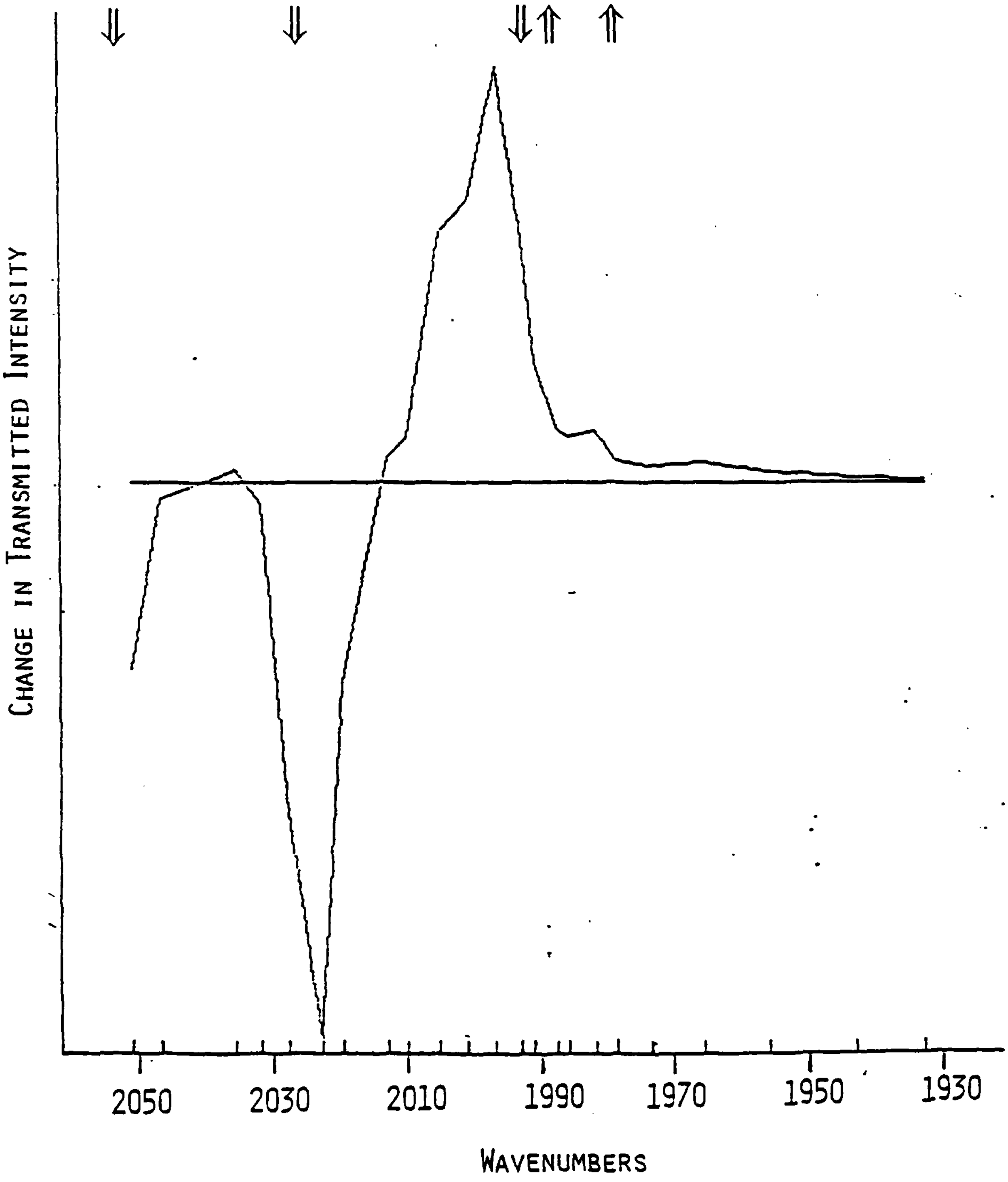
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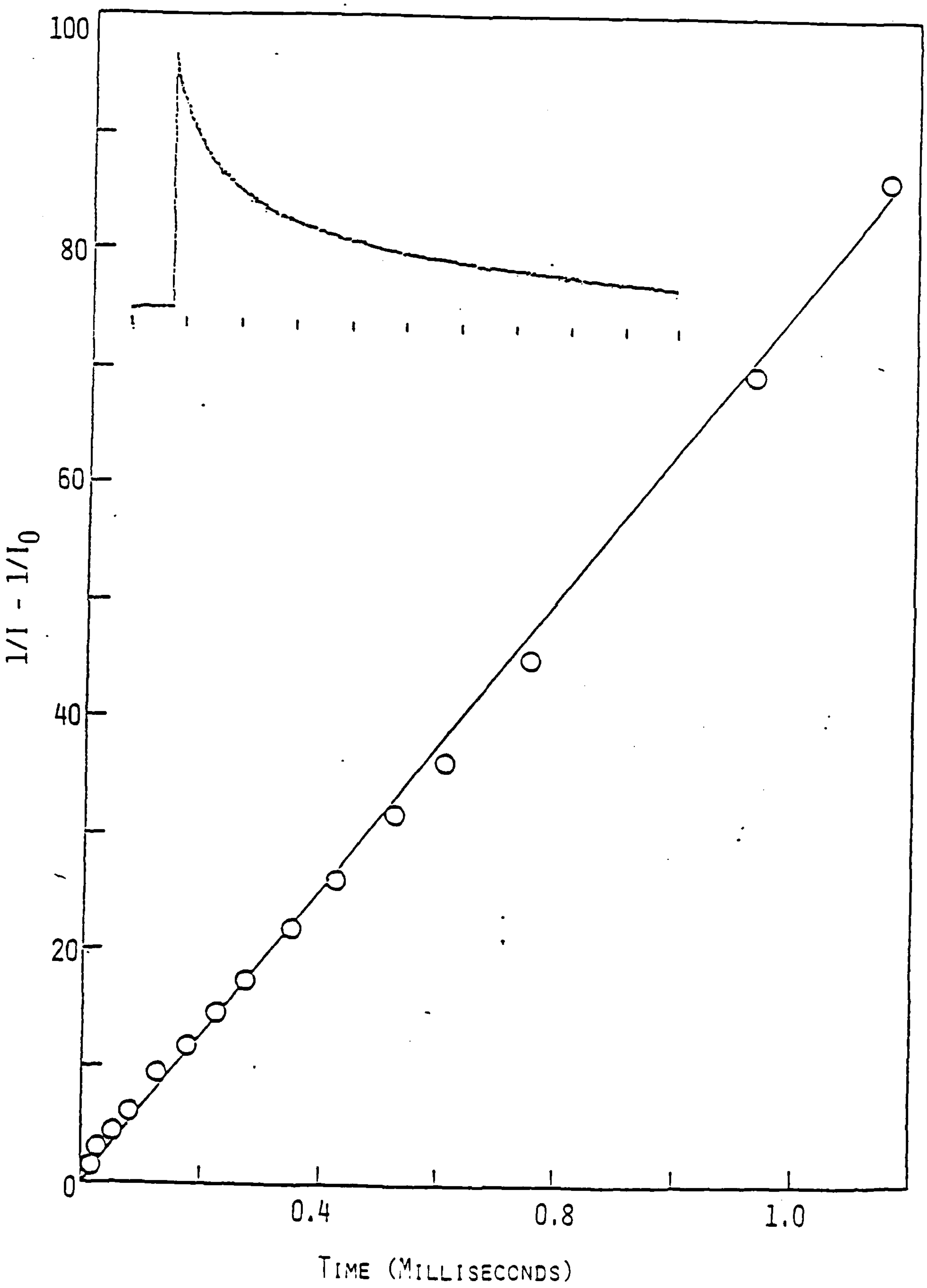
Figure 2



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