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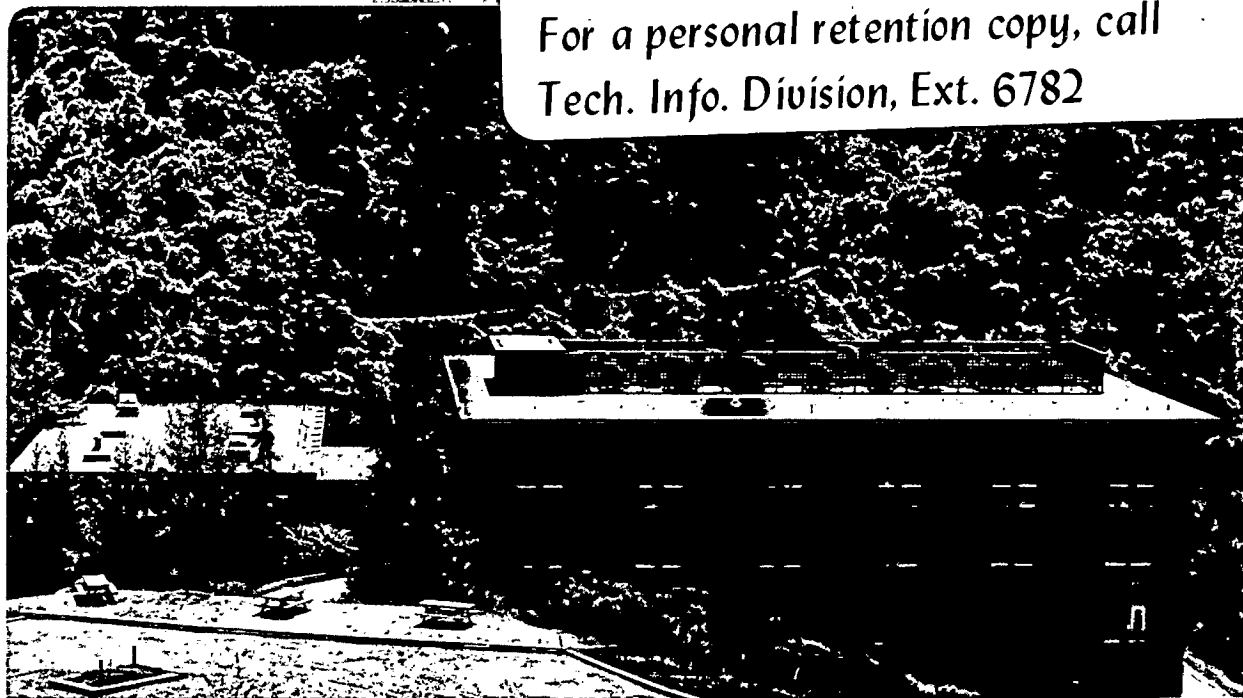
THE REACTION OF FORMYL RADICALS WITH NO AND O₂:
ABSOLUTE RATE CONSTANTS AND KINETIC ISOTOPE EFFECTS

Andrew O. Langford and C. Bradley Moore

December 1981

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The Reaction of Formyl Radicals with NO and O₂:
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Absolute Rate Constants and Kinetic Isotope Effects  
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ABSTRACT

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Absolute rate constants for the reactions  $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$ ,  $\text{DCO} + \text{O}_2 \rightarrow \text{DO}_2 + \text{CO}$ ,  $\text{HCO} + \text{NO} \rightarrow \text{HNO} + \text{CO}$ , and  $\text{DCO} + \text{NO} \rightarrow \text{DNO} + \text{CO}$  have been measured at  $295 \pm 2\text{K}$ . The technique of laser resonance absorption in conjunction with laser photolytic generation of formyl was used to obtain values of  $(4.8 \pm 0.7) \times 10^{-12}$ ,  $(5.3 \pm 0.7) \times 10^{-12}$ ,  $(1.24 \pm 0.2) \times 10^{-11}$ , and  $(1.62 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , respectively, for these reactions. The indicated errors are two standard deviations in the linear least-squares treatment of the pseudo-first-order rate constants. A qualitative model based on the formation and subsequent unimolecular decay of a long-lived collision complex is proposed to explain the observed isotope effects.

## INTRODUCTION

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The gas phase oxidation of virtually all hydrocarbons involves the formation and reaction of formyl radicals.¹ Since hydrocarbon oxidation processes are important both in combustion and atmospheric chemistry, reliable absolute rate constant values are essential for a detailed understanding and accurate modelling of these systems.

Relatively few measurements of formyl radical reaction rates have been made since time-resolved detection of the radical is difficult. Predissociation following electronic excitation has limited optical detection to absorption techniques. Recently, both intracavity dye laser spectroscopy (IDLS)²⁻⁴ and flash spectroscopy (FS)⁵ have been used to detect formyl radicals with considerable success. For kinetic studies, however, laser resonance absorption (LRA) with a cw dye laser provides a more effective technique since continuous detection is possible.⁶

The detection of transient species by resonance absorption using CW lasers is a logical extension of more conventional kinetic absorption techniques. The collimation of the laser beam permits long absorption path lengths in small volume cells. Laser linewidths narrower than most absorption features and well-defined beam geometries make it easy to relate absorption intensities to relative radical concentrations. Narrow linewidths also make it easier to minimize absorption by other

species and with a tunable laser permits the acquisition of kinetic spectra. When used in conjunction with laser photolysis, transients can be detected on time scales comparable to the laser pulse, typically 10^{-8} s.

In this study, a tunable cw dye laser has been used to detect ground state formyl radicals, HCO and DCO, produced in the ultraviolet laser photolysis of formaldehyde (H_2CO or D_2CO). Rate constants for the following reactions have been determined at 295K.



The observed kinetic isotope effects are qualitatively explained via a simple collision complex model.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Figure 1. The photolysis cell was constructed entirely of quartz, 3 cm i.d. x 35 cm long with $\lambda/4$ flat quartz windows

sealed on at Brewster's angle (visible) using glass transfer tape (Vitta Corp G-105). Frequent heating of the cell under vacuum with a gas-oxygen flame prevented excessive polymerization of the formaldehyde even at a pressure of 20 torr. Two teflon stopcocks isolated the cell from the vacuum system.

Formyl radicals were produced by photolysis of formaldehyde (H_2CO , D_2CO) with a XeCl laser (Lumonics TE-262). The laser output consists of two equally intense lines at 308.0 and 308.2 nm. It was operated with a total of 10-30 mJ in a 12 nsec FWHM pulse at a repetition rate of 1-5 Hz. The cross-sectional area of the beam was $\sim 6 \times 20 \text{ mm}^2$ at the laser and $\sim 7 \times 25 \text{ mm}^2$ through the cell to give an energy fluence of 5-15 mJ/cm^2 after losses. The beam was collimated with a 1m f.l. quartz lens and coupled into the cell by a 45° incidence UV high reflector ($R > 98\%$) with $> 97\%$ transmission in the visible.

The absorption coefficients of H_2CO and D_2CO for XeCl radiation (both lines) were measured to be $(3.3 \pm 0.3) \times 10^{-4}$ and $(8.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1} \text{ torr}^{-1}$ respectively. The resulting absorbance over the length of the cell was 4.5% for 4.0 Torr H_2CO and 5.5% for 2.0 Torr D_2CO , typical pressures used in these experiments. Using a quantum yield⁷ for radical production of 0.5 and 0.4 for H_2CO and D_2CO respectively, the initial radical concentrations were estimated as $[\text{HCO}]_0 = 1.5 \times 10^{13}$ and $[\text{DCO}]_0 = 3.5 \times 10^{13} \text{ molec}/\text{cm}^3$ per pulse for 15 mJ/cm^2 at the above formaldehyde pressures. Although the experiments were performed under static conditions, depletion of the reactants through photolysis was always less than 5%.

An Ar⁺ pumped, ring dye laser (Spectra-Physics UV-171/380c) with a linewidth of <3GHz was used to detect formyl radicals. Absorptions within the R branch of the $\tilde{A}^2A''(0,9,0) + \tilde{X}^2A'(0,0,0)$ transition of HCO near 6138Å or the $\tilde{A}^2A''(0,13,0) + \tilde{X}^2A'(0,0,0)$ transition of DCO near 5842Å were probed.⁸

The laser wavelength was determined to within $\pm 0.1\text{\AA}$ with a Jobin-Yvon 1.5m monochromator calibrated to a Ne line standard. The probe beam was collimated to a diameter of 2mm by a telescope, and passed 7 times through the cell within the reaction volume defined by the photolysis beam and $7 \times 25\text{mm}^2$ rectangular apertures external to the cell. The power of the probe laser within the cell was typically 20-80mW.

After attenuation to 10-20mW, the beam was focussed onto a fast photodiode (EGG SGD 100A) coupled to one input of a wideband (DC-10MHz) differential amplifier. A small fraction (~3%) of the beam was split off before the cell by a glass slide and focussed onto an identical photodiode connected to the other amplifier input. Fluctuations in the dye laser (~10% on microsecond time scales) amplitude were thus reduced by about one order of magnitude.

The signal from the amplifier was digitized by a Biomation 8100 transient digitizer used in conjunction with a Northern NS-575A multichannel analyzer to permit signal averaging. The data was then stored on magnetic tape and transferred to floppy diskette for analysis with an LSI-11 mini-computer.

Formaldehyde was prepared according to the method of Spence and Wild⁹ and was stored at 77K to prevent polymerization. O₂

(Baker UHP 99.995%), Ar (Matheson UHP 99.999%) and N₂ (LBL 99.999%) were used without further purification. NO (Matheson 99.0%) was purified by distillation through a silica gel trap kept at 195K and subjected to repeated freeze-pump-thaw cycles at 77K to remove NO_x impurities. The liquified product of such a procedure was bright blue with no trace of yellow or green coloration from NO_x impurities. All gases were kept in vessels with greaseless stopcocks and transferred to the photolysis cell using a standard vacuum line with a base pressure of less than 1×10^{-6} Torr. Pressure measurements ($\pm 0.3\%$) were made with either a capacitance manometer (MKS Baratron P < 10 Torr) or a variable reluctance manometer (Validyne P < 50 Torr). All experiments were performed at an ambient temperature of 295 ± 2 K.

RESULTS

Analysis. The decay of HCO in 4.0 Torr H₂CO is shown in Figure 2. The removal of H and HCO radicals in the absence of NO or O₂ occurs through reactions (5)-(7).²



In order to extract the rate constants k_1 - k_4 from the experimental data, the possible effects of these competing reactions must be considered. The complete kinetic scheme for the H₂CO-NO/O₂ systems has been described in considerable detail by Reilly et.al.,² and will not be repeated here. Since the ratios $\frac{[\text{NO}/\text{O}_2]}{[\text{HCO}]}$ and $\frac{[\text{NO}/\text{O}_2]}{[\text{DCO}]}$ were always greater than 100 (typically = 1000) in this study, the decay of HCO became 2 to 3 orders of magnitude faster (Figure 3) than the decay in pure formaldehyde (Figure 2). Under these conditions, reactions (5) and (6) could be neglected and k_1 - k_4 determined by pseudo-first order analysis.

Rate Constants. The pseudo-first-order rate constants for reactions (1)-(4) are plotted as a function of oxidant pressure in Figures 4 and 5. The error bars on the experimental points represent the extreme values of the exponential fit within the noise of the decay traces. Any deviations due to radical-radical

reactions should be well within these limits. The data shown in these figures are presented in Table I. The rate constants k_1 - k_4 were obtained from a linear least-squares fit of this data. The error limits on the reported rate constants are two standard deviations ($k \pm 2\sigma$). These results are compared with previously reported values in Table II.^{2-6,10}

Kinetic Isotope Effects. One unexpected result of this study is that DCO reacts with NO and O₂ faster than HCO. This result can be used to infer mechanistic information about the elementary reaction (see Discussion). The observed isotope effects are $k_H/k_D = 0.78 \pm 0.05$ and 0.90 ± 0.10 for the reactions with NO and O₂ respectively. The error bars on these quantities reflect the probable systematic nature of the significant sources of experimental error, i.e. error sources which have a similar effect on HCO and DCO measurements and cancel out in the ratio k_H/k_D .

DISCUSSION

Evaluation. The rate constants which have now been reported for reactions (1)-(4) are listed in Table II. The values of k_3 obtained in three previous studies are in excellent agreement with the present result. Although Shibuya et.al.⁵ reported a value approximately 30% lower, the results of four studies indicate that $k_3 \sim 1.2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Such good agreement is not unexpected since these results were obtained using similar techniques which monitored photolytically generated HCO via the visible $\tilde{A} + \tilde{X}$ absorption. It is therefore surprising that the values of k_1 obtained by the same methods range from 3.7 to $5.6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, a variation of 50%.

Since the rate constants obtained in earlier studies^{2,4,5} were extracted from kinetic models which included radical-radical reactions such as (5) and (6), inaccuracies in the assumed values for these rate constants would become more apparent in the oxygen system where these reactions make a greater contribution to the overall decay. The use of pseudo-first-order conditions in the present study eliminated this possible source of error.

Complications in the formaldehyde photo-oxidation system may also affect measurements of k_1 . When static mixtures were repeatedly irradiated in a recent study by Veyret and Lesclaux⁶, a shot-to-shot decrease in the first-order rate constant, $k_1[\text{O}_2]$, was observed and attributed to depletion of the oxygen through HO_2 initiated chain reactions.

Such depletion was proposed as an explanation for the lower

values of k_3 observed in studies based on intracavity detection of HCO.^{2,4} This explanation may not be correct, however, since the extent of chain reaction increases strongly as the aldehyde to oxygen ratio increases,¹¹ this ratio was about an order of magnitude greater in Veyret's and Lesclaux's experiments than in the intracavity work (~250 compared to ~25). Uncertainties in the radical-radical rate constants are a more likely source of error in the intracavity experiments.

Although static mixtures were irradiated by hundreds of laser pulses in the present study to permit signal averaging, depletion effects were not observed for oxygen pressures greater than 0.5 Torr and hence did not affect the rate constant determination ($\frac{[H_2CO]}{[O_2]} < 10$). At pressures less than 0.3 Torr, however, a decrease in the rate constant (~10%) was observed, presumably due to this effect. The value of k_1 determined in Ref. 6 (which also used laser resonance absorption) differs from the present result by only 15% - within the combined error bars.

Rate constants for the DCO analogues of these reactions, k_2 and k_4 , are reported here for the first time.

Reaction Mechanism. The products of reactions (1)-(4) were not directly observed in this study. Although the indicated products are well established from previous work,^{2,12} the existence of a collisionally stabilized addition reaction to form HCOO₂ (or HCNO) has also been proposed.¹³ Since earlier measurements of k_1 indicate that the rate constant is pressure independent (at least up to ~500 Torr)^{4,5,6} contributions from an addition

channel can not be very important.

The formation of HO₂ and HNO in reactions (1) and (3) respectively, is consistent with a simple hydrogen abstraction mechanism. Assuming such a mechanism, calculations using the method developed by Bigeleisen and coworkers¹⁴ (based on transition state theory) predict a moderate normal isotope effect ($k_H/k_D = 3.4$) for the formyl-nitric oxide reaction.¹⁵ Since the observed isotope effects are inverted, direct abstraction seems unlikely. Furthermore, the decrease in rate constant with increasing temperature⁶ demonstrates that the activation energy is too close to zero for a direct hydrogen abstraction.

The temperature dependence indicates that the reactants are brought together by attractive forces and proceed to products without encountering a barrier above the energy zero of reagents. The inverted isotope effect may be understood if H is more tightly bound in the transition state than in the reactants.¹⁶ One possible explanation for these observations is the formation and subsequent decomposition of a "long-lived" collision complex (Figure 6).

Such a complex may be formed via a "loose" transition state as has been proposed for methyl recombination.¹⁷ This complex may then dissociate to form either reactants or product. The lifetime of the complex must be equal to many vibrational periods ($\sim 10^{-12}$ s), but shorter than $\sim 2 \times 10^{-10}$ s to prevent collisional stabilization below 500 Torr (assuming strong collisions). At low collision energies, the rate of formation of the complex is essentially the gas kinetic collision rate which has a negligible

isotope dependence. The isotope effect therefore arises from the relative efficiencies for decomposition of the complex to form reactants and products.¹⁸ If, for example, when the C-H stretching frequency in the transition state is greater than the anomalously low 2488 cm^{-1} of HCO,^{19,20} the barrier to product formation relative to the threshold for dissociation to reactants is higher for H than for D (Figure 6).

Although such a mechanism can qualitatively explain the experimental results, a quantitative description using RRKM theory has not been possible since no *a priori* knowledge of the structures and vibrational frequencies of the transition states and collision complex exist. RRKM calculations using frequencies and structures based on analogy with stable molecules were attempted but proved inconclusive.

SUMMARY

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In this work, laser resonance absorption has been used to monitor the decay of formyl radicals produced through the photodissociation of formaldehyde. Room temperature rate constants for the reactions of HCO or DCO with NO and O<sub>2</sub> have been measured and a collision complex mechanism is proposed to explain the observed isotope effects. Attempts to quantitatively test this mechanism using RRKM theory were limited by the lack of *a priori* knowledge of the vibrational frequencies and structures of the collision complex and transition states. *Ab initio* calculation of these quantities may make such a test possible. Further experimental studies to determine the effect of internal excitation of the formyl radicals on these reaction rates are planned.



Acknowledgements  
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TABLE I: Rate Data for Reactions (1)-(4) at 295K

Oxidant (Torr)	Formaldehyde (Torr)		Laser shots @ 10 mJ/cm ²	Decay Rate x 10 ⁻⁵ s ⁻¹	k x 10 ¹² cm ³ molec ⁻¹ s ⁻¹	
1.00	O ₂	4.01	H ₂ CO	512	1.45 ± 0.1	4.59
1.20		4.03		256	1.8 ± 0.2	4.75
1.24		3.78		512	1.85 ± 0.3	4.72
1.40		4.21		256	2.2 ± 0.2	4.97
1.50		3.55		512	2.3 ± 0.2	4.85
1.80		4.22		512	3.0 ± 0.5	5.27
2.00		4.06		256	3.0 ± 0.2	4.75
2.60		3.10		256	3.7 ± 0.3	4.50
3.00		7.0		512	4.4 ± 0.3	4.64

$$(k_1 \pm 2\sigma) = (4.8 \pm 0.7) \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

1.00	O ₂	2.0	D ₂ CO -	128	1.7 ± 0.2	5.38
1.10		2.02		128	2.0 ± 0.2	5.75
1.40		2.03		128	2.2 ± 0.2	4.97
1.80		2.16		128	2.7 ± 0.2	4.75
2.00		2.12		128	3.3 ± 0.2	5.22
2.40		2.03		128	3.6 ± 0.3	4.75
2.60		2.02		128	4.5 ± 0.3	5.48
2.80		1.99		128	5.0 ± 0.3	5.65
3.20		2.03		256	5.5 ± 0.3	5.44

$$(k_2 \pm 2\sigma) = (5.3 \pm 0.7) \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

0.300	NO	3.20	H ₂ CO	256	1.3 ± 0.3	13.7
0.400		3.61		256	1.7 ± 0.3	13.4
0.595		3.05		512	2.7 ± 0.3	14.4
0.701		3.30		256	2.65 ± 0.3	12.0
0.806		3.40		256	2.9 ± 0.3	11.4
0.901		4.12		256	3.5 ± 0.3	12.3
1.051		4.10		512	3.55 ± 0.3	10.7
1.148		3.87		512	4.3 ± 0.3	11.85
1.308		3.71		512	4.9 ± 0.3	11.85

$$(k_3 \pm 2\sigma) = (1.24 \pm 0.2) \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

0.300	NO	2.40	D ₂ CO	128	1.6 ± 0.3	16.9
0.405		2.40		64	1.95 ± 0.3	15.2
0.501		2.50		128	2.6 ± 0.3	16.4
0.602		2.60		64	3.2 ± 0.3	16.8
0.750		2.92		128	3.55 ± 0.3	15.0
0.801		2.81		128	4.1 ± 0.3	16.2
0.902		2.90		128	4.5 ± 0.3	15.8
1.000		2.99		128	5.4 ± 0.3	17.1
1.305		4.90		128	6.7 ± 0.3	16.25

$$(k_4 \pm 2\sigma) = (1.62 \pm 0.2) \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$$

TABLE II. SUMMARY OF REPORTED RATE CONSTANT VALUES AT ROOM TEMPERATURE

$k_1 \times 10^{12}{}^a$	$k_2 \times 10^{12}{}^a$	$k_3 \times 10^{11}{}^a$	$k_4 \times 10^{11}{}^a$	Method ^b	Reference
5.7 ± 1.2^c	-	-	-	DF/MS	10
5.6 ± 0.9	-	$.85 \pm .1$	-	FP/FS	5
4.0 ± 0.8	-	$1.4 \pm .2$	-	LP/IDLS	2
3.7 ± 0.8	-	1.2	-	FP/IDLS	4
5.6 ± 0.6	-	$1.23 \pm .12$	-	FP/LRA	6
4.2 ± 0.7	-	-	-	FP/IDLS	3
4.8 ± 0.7	5.3 ± 0.7	$1.24 \pm .2$	$1.60 \pm .2$	LP/LRA	This Work

^a $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$.

^b DF/MS, discharge flow with mass spectrometry detection; FP/FS, flash photolysis with flash spectroscopy detection; LP/IDLS, laser photolysis with intra-cavity dye laser detection; LP/LRA, laser photolysis with laser resonance absorption detection.

^c k_1 measured relative to rate constant for $\text{HCO} + \text{O}$ reaction, $k = (2.1 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$.

Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Decay of HCO in 4.0 Torr H₂CO averaged for 128 laser shots at 10 mJ/cm². The solid line corresponds to a kinetic fit based on the ratio $k_5/k_6 = 7.0$.

Figure 3. Decay of HCO in 4.0 Torr H₂CO with 1.00 Torr O₂ added. The solid line corresponds to a pseudo-first-order rate constant of $1.45 \times 10^5 \text{ s}^{-1}$ ($k_1 = 4.6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$).

Figure 4. Pseudo-first-order rate constants for reactions (1) and (2) as a function of oxygen pressure. The dashed line in the upper graph corresponds to the rate constant for reaction (1).

Figure 5. Pseudo-first-order rate constants for reactions (3) and (4) as a function of nitric oxide pressure. The dashed line in the upper graph corresponds to the rate constant for reaction (3).

Figure 6. Schematic potential energy diagram for the collision complex mechanism for reactions (3) and (4). The potential well depth of $\sim 45 \text{ kcal mol}^{-1}$ and exothermicity of $\sim 28 \text{ kcal mol}^{-1}$ ($\sim 26 \text{ kcal mol}^{-1}$ for O₂ reactions) are estimated from standard thermochemical data and $\Delta H_f^\circ(\text{HCO}) = 8 \text{ kcal mol}^{-1}$.

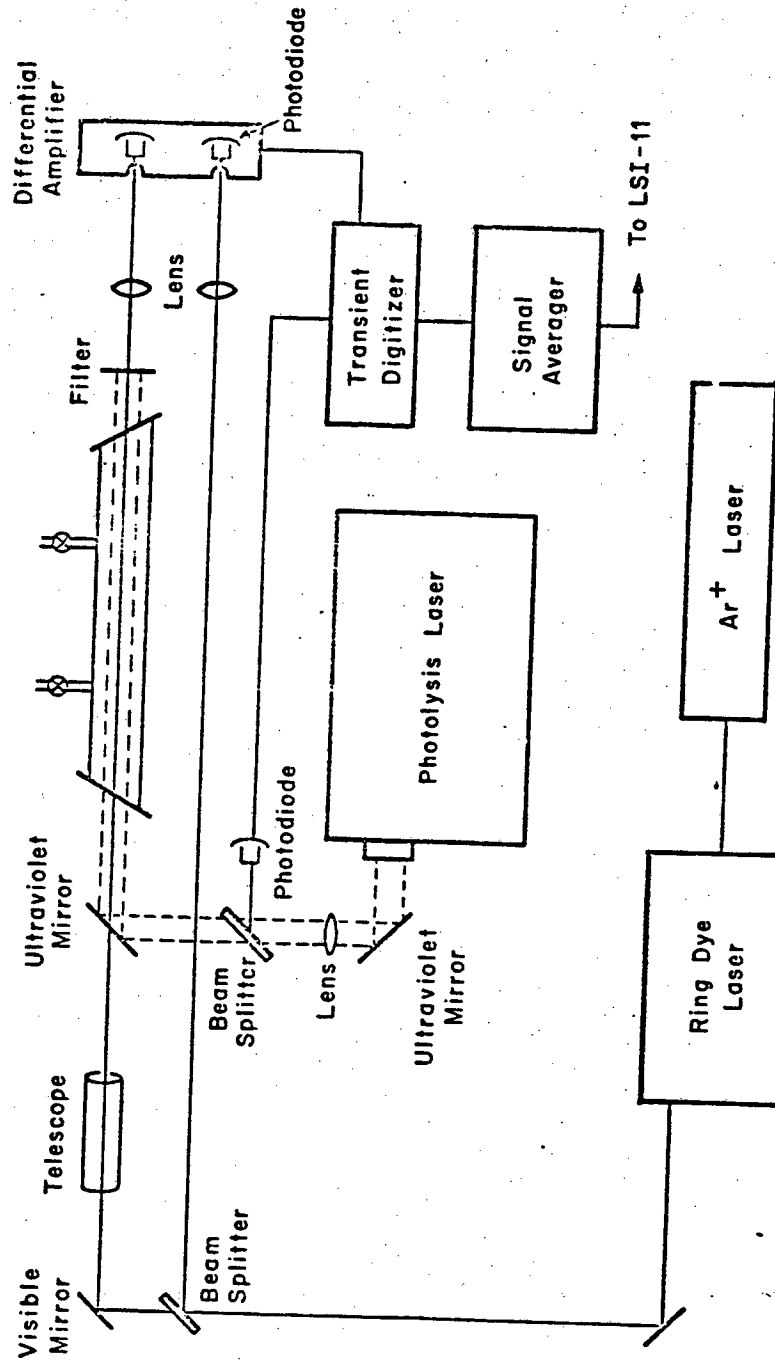


Fig. 1

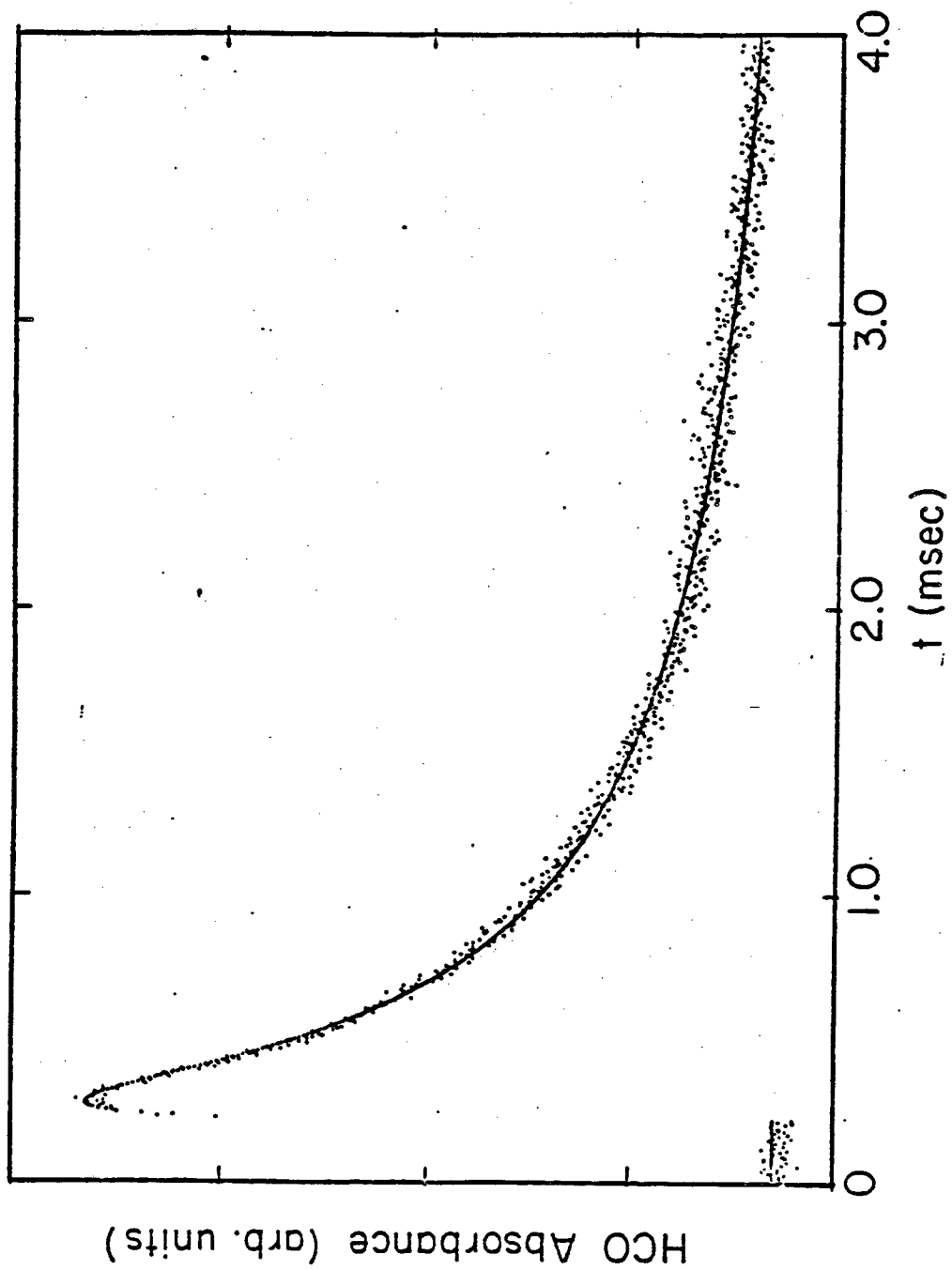


Fig. 2

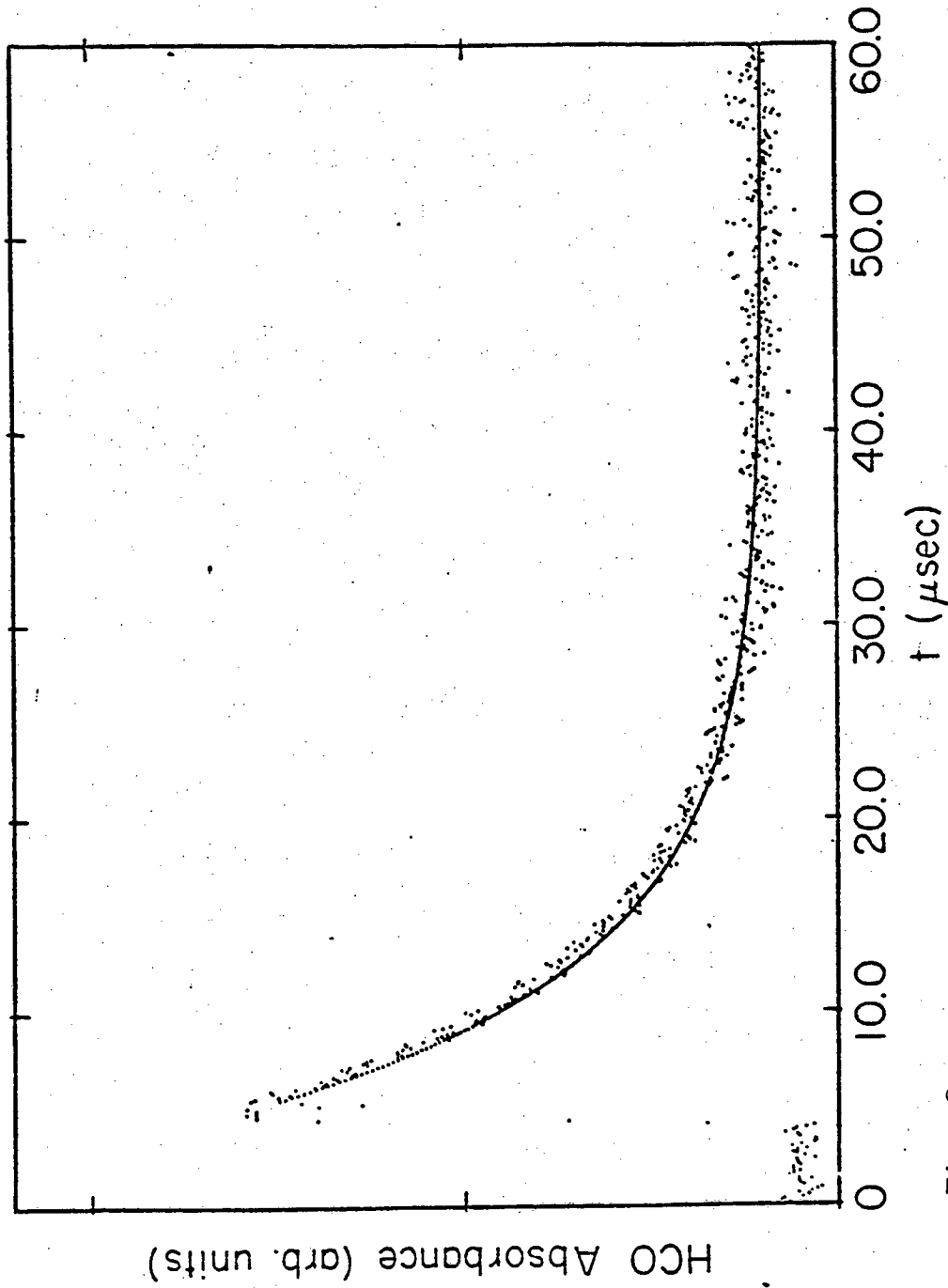


Fig. 3

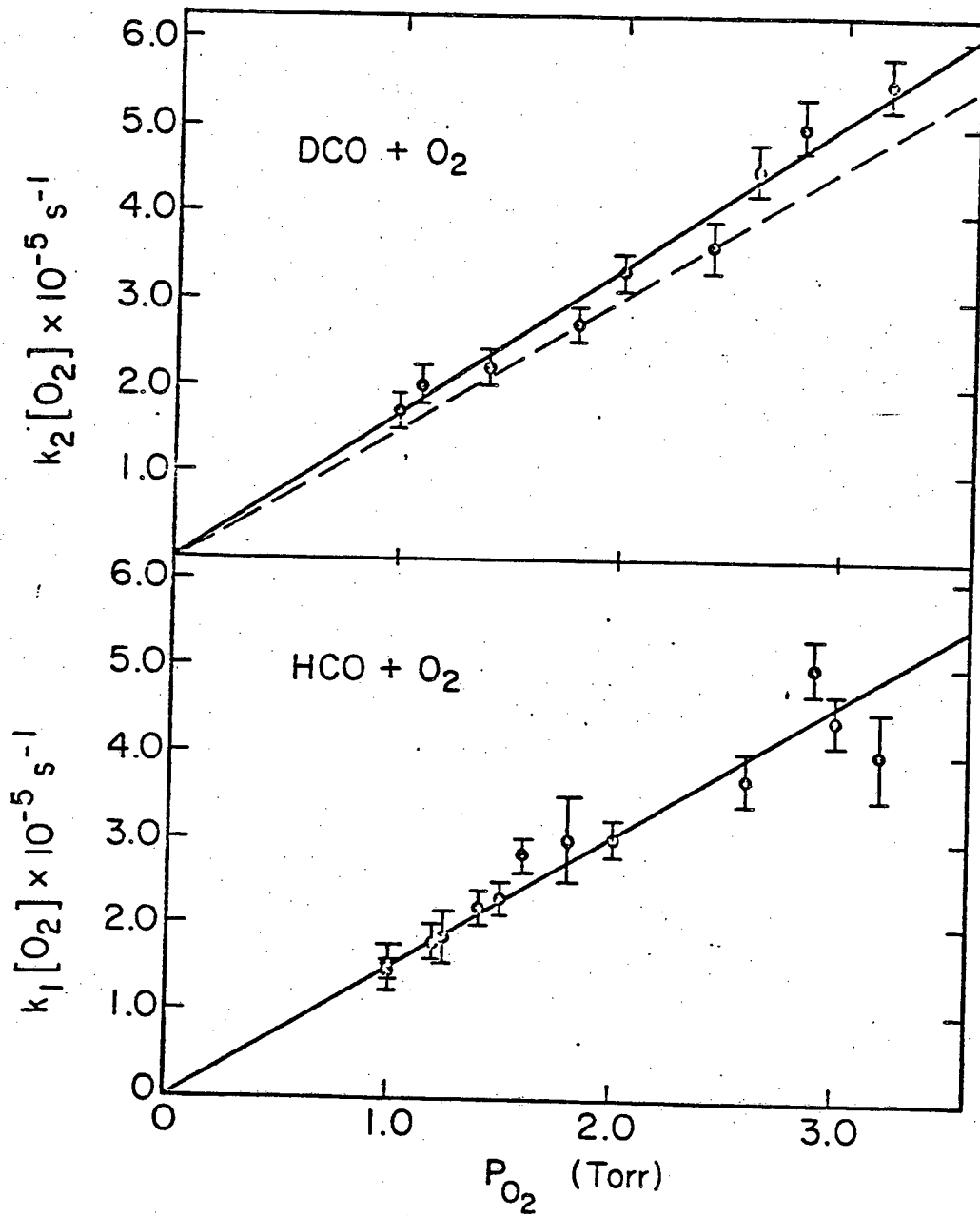


Fig. 4

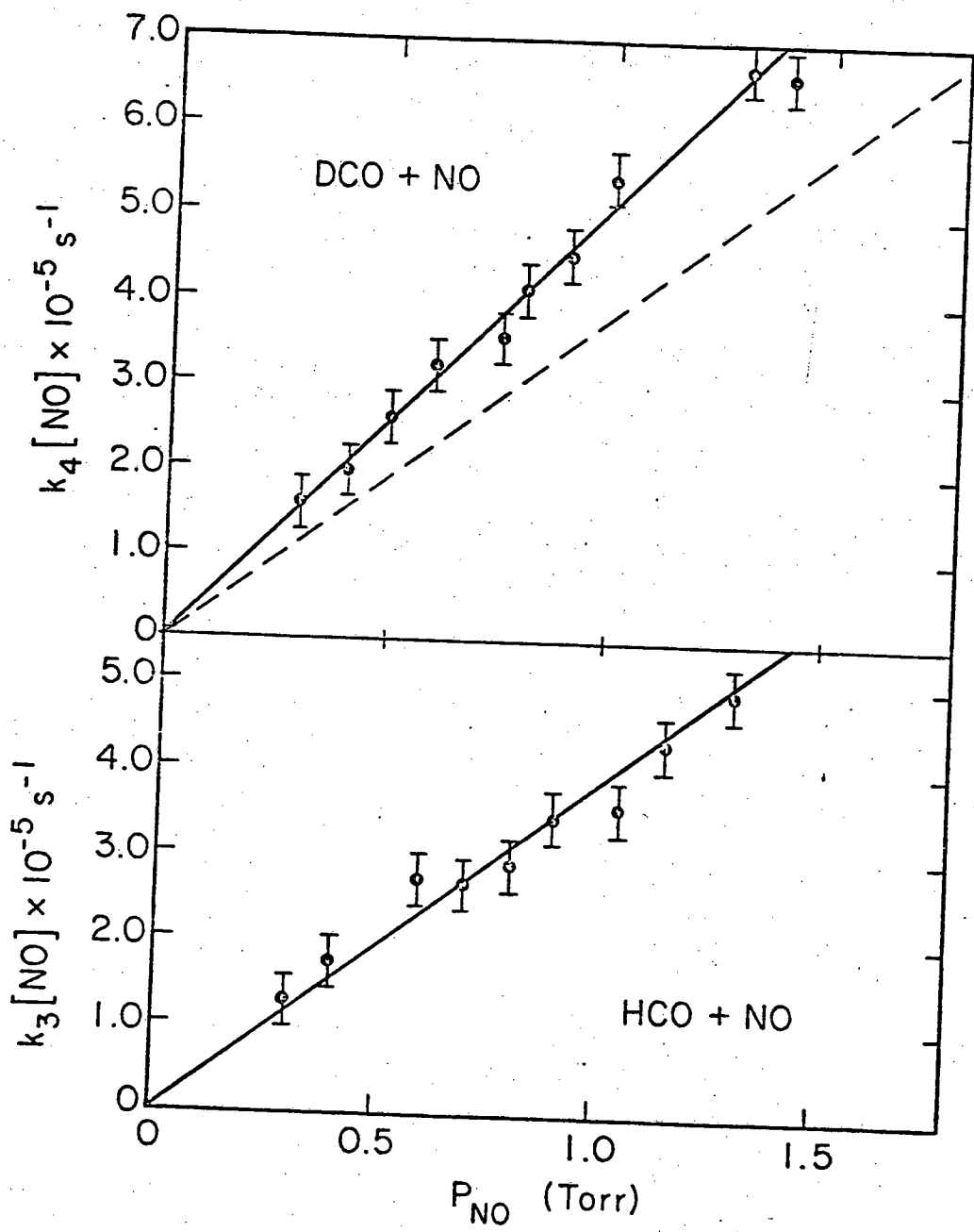


Fig. 5

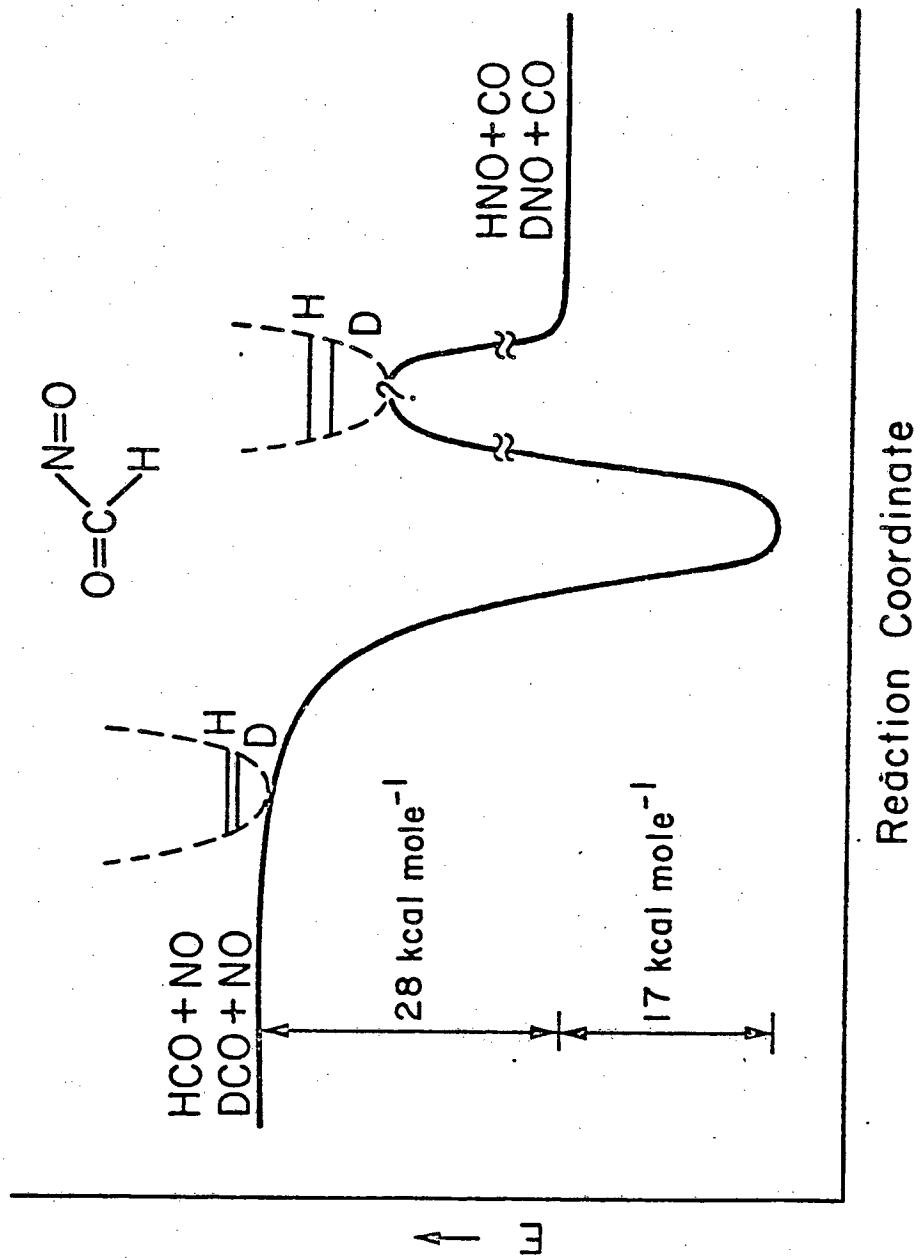


Fig. 6

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