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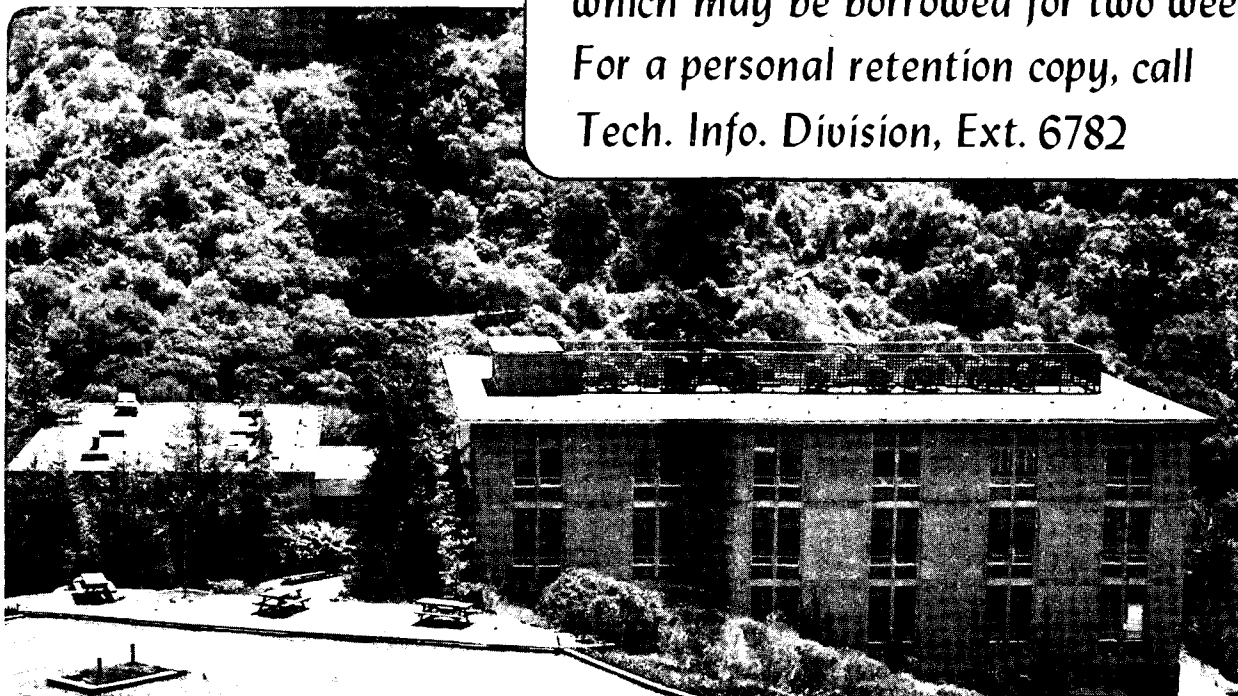
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Michael J. Wax and Robert G. Bergman

September 1981

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DIRECT EVIDENCE FOR SOLVENT COORDINATION IN MIGRATORY CO INSERTION

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Abstract

The role of solvent in phosphine-induced migratory CO insertion in $\text{Cp}(\text{CO})_3\text{MoCH}_3$ (1, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has been investigated, using tetrahydrofuran (THF) and methyl-substituted THF solvents with similar polarities but different coordinating abilities. For PMePh_2 in THF, kinetic studies reveal two parallel pathways, one (governed by k_3) dependent upon $[\text{PMePh}_2]$, and the other (governed by k_1) saturating in phosphine. Similar behavior is found in 3-methyltetrahydrofuran (3-MeTHF). In 2-MeTHF, however, k_1 is decreased significantly, and is depressed further in 2,5-Me₂THF, while these solvents leave k_3 unchanged. These observations suggest strongly that the k_1 path involves coordination of solvent to molybdenum in the migratory insertion transition state, thus arguing against a generalized solvation effect linked to solvent dielectric constant. In support of this conclusion, a first-order dependence of k_1 on THF concentration has been demonstrated by using varying amounts of that solvent in 2,5-Me₂THF.

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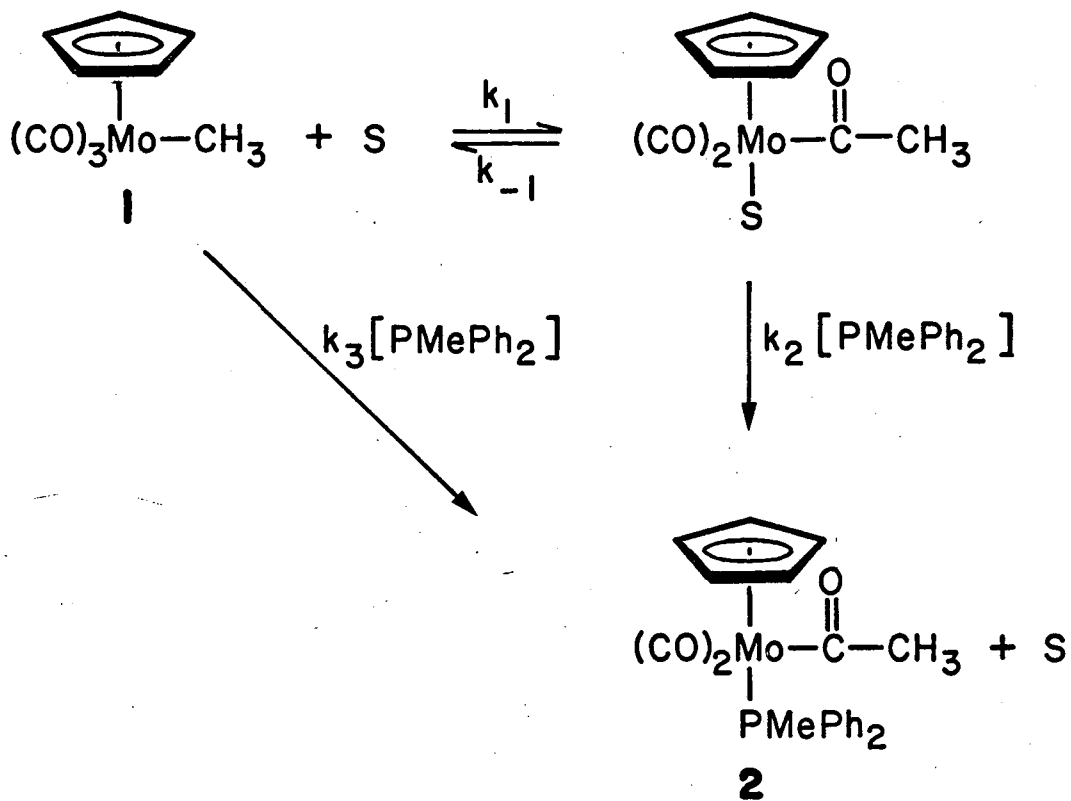
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Migratory CO insertion, perhaps the most thoroughly studied process in organotransition metal chemistry,¹ is subject to solvent effects which in some cases are quite large. In early work on the carbonylation of pentacarbonylmethylmanganese(I), Calderazzo and Cotton² observed enhanced rates in polar, donating solvents which they attributed to variations in dielectric constant. Since that time, other systems have been found to exhibit similar behavior.¹ The stereochemistry of CO migratory insertion also is affected markedly by changes in solvent. As Flood and his coworkers have pointed out recently,³ two conflicting explanations have been postulated for these effects: (a) generalized stabilization of the migratory insertion transition state by solvation, and (b) direct attack of solvent at the metal center. Neither experimental work nor semi-empirical theory⁴⁻⁶ has provided a convincing means of distinguishing between these two models.

Complicating interpretation of rate data are changes in kinetic order encountered when alkylcarbonyl complexes are treated with nucleophiles in various solvents. Butler, Basolo, and Pearson found that the rate of reaction of $\text{CpMo}(\text{CO})_3\text{CH}_3$ (1, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) is a linear function of triphenylphosphine concentration in benzene, but is independent of the amount of phosphine present in tetrahydrofuran (THF).⁷ In chloroform, both of these types of behavior are exhibited simultaneously by the ethyl analog of 1.⁸ Pentacarbonylmethylmanganese(I) reacts according to either first or second

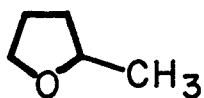
Scheme 1



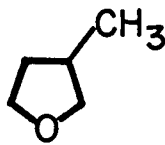
(S = solvent)



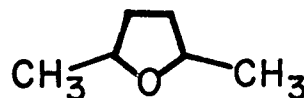
THF



2-MeTHF



3-MeTHF



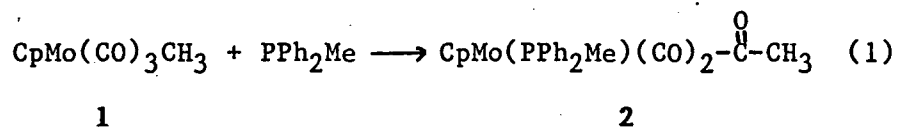
2,5-Me₂THF

order or saturation kinetics, depending upon the nucleophile and solvent used.⁹

The cyclopentadienyltricarbonyl(alkyl)molybdenum insertion has been the object of intense study and displays large medium effects. In this paper we report the application of a technique to this system which distinguishes between the two solvent-involvement models mentioned above. We believe our results offer the first truly compelling support for the original hypothesis of Mawby, Basolo and Pearson¹⁰ that in this case the effect of solvent can be explained only in the context of direct attack of donor solvents at the metal center as the alkyl migration is occurring. In other words, these migrations are "solvent-catalyzed".

Separation of donor and polarity effects in solvent-influenced reactions is hindered by the relatively high nucleophilicity which often is exhibited by polar solvents. In order to avoid this difficulty, we have confined our studies to a series of methyl-substituted tetrahydrofurans (Scheme 1), which would be expected to vary widely in donicity¹¹ but not in dielectric constant.¹²

Shown in equation 1 is the specific reaction under examination, chosen because of our interest in it as a model for related processes¹³ involving the reaction of metal hydrides with 1, and because of its similarity to



reactions studied by others.^{7,8,10} When 1 is allowed to react with varying (but at least five-fold molar excess) concentrations¹⁴ of diphenylmethylphosphine in THF at 60 °C, production of $\text{CpMo(CO)}_2(\text{PMePh}_2)\text{COCH}_3$ ¹⁵ (2) is seen to occur concomitant with first order disappearance of starting material.¹⁶ A plot of observed rate constant

versus nucleophile concentration for this reaction (Figure 1) indicates superimposed saturation and second order kinetics (eq. 2). The same rate law, and similar rate constants, are obtained in 3-methylTHF (Fig. 1, Table

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{PMePh}_2]}{k_{-1} + k_2 [\text{PMePh}_2]} + k_3 [\text{PMePh}_2] \quad (2)$$

1), supporting the idea that the electronic effect of the added methyl group is small.¹²

Simpler behavior is seen in 2-MeTHF, namely, parallel first- and second-order paths (Figure 1). The value of the second-order rate constant k_3 is essentially unchanged from that in THF, whereas k_1 (defined by the non-zero intercept in Figure 1) is significantly diminished (Table 1). An even greater decrease in k_1 , with no change in k_3 , is observed on using a 2,5-dimethyltetrahydrofuran¹⁷ (2,5-Me₂THF) medium. The simplest explanation for the linearity here is that in both 2-substituted solvents the rate law is still that given in eq. (2), but k_2/k_{-1} has become sufficiently large to prevent the saturation route from entering a second-order regime at low phosphine concentrations.

Given the similarity in dielectric constants of methyl-substituted THF's, the only rational explanation for the effect of α -methyl substitution on k_1 is steric hindrance to direct coordination of THF to molybdenum in the transition state for migratory insertion. One consequence of this conclusion may be probed: the rate of the solvent-assisted pathway should be first-order in the concentration of solvent itself (that is, k_1 is actually the product of a second-order rate constant k_1' and the solvent concentration). The near equality in dielectric constant of THF and 2,5-Me₂THF has allowed us to test this prediction. In Figure 3 are plotted the k_1 values obtained from studies of the reaction of 0.01 M 1 with varying concentrations of PMePh₂ in

THF/2,5-Me₂THF mixtures. As these data demonstrate, k_1 is a linear function of [THF] over the entire mole fraction range (0 to 1.0), with $k_1' = 6.21 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$.

It should be noted that the k_2 step also must involve direct phosphine attack; i.e., it is an S_N2 displacement of solvent by phosphine. A dissociative mechanism for this step would proceed through a coordinatively unsaturated acyl (or perhaps η^2 -acyl) complex. It is difficult to see why such an intermediate would not also be accessible directly from 1; our results show that it is not.

The results described here are understandable only in terms of direct coordinative solvent assistance to migratory CO insertion. This hypothesis provides a satisfying explanation for the large solvent effects which have been observed on the rate of this reaction in several different complexes.¹⁸ Our conclusions may not apply to systems such as CpFe(CO)₂R, in which solvent effects are small. Amusingly, in the iron system a solvent-coordinated acyl complex actually is formed in dimethylsulfoxide,¹⁹ but Nicholas, Raghu and Rosenblum have suggested that this complex is not on the path from alkyl to phosphine-substituted acyl.^{19,20} It is perhaps important to realize, therefore, that direct observation of such an "intermediate" is not always compelling evidence for its involvement in a reaction mechanism. In any event, in cases similar to the molybdenum system where large solvent effects on rates are observed, we hope that α -substituted THF's will be useful in separating polarity and direct coordination properties of ethereal solvents.

Acknowledgments. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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- (12) The visible absorption maximum of indigo, a positive solvatochromatic dye, in all of these solvents is 601 ± 1 nm (compared with 588 nm in chloroform and 620 nm in DMSO¹¹), indicating that they have comparable polarities.
- (13) Jones, W.D.; Bergman, R.G. J. Am. Chem. Soc. 1979, 101, 5447-5449.
- (14) A typical concentration range was from 0.023 to 1.00 M.
- (15) Data for 2: IR(THF) 1938 s, 1851 vs, 1627 m cm^{-1} ; $^1\text{H-NMR}$ (benzene- d_6) δ 7.47-6.89 (m, 10H), 4.57 (d; $J = 1.9$, 5H), 2.90 (s, 3H), 1.75 (d, $J = 8$, 3H); Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{MoO}_3\text{P}$: C, 57.40; H, 4.60. Found: C, 57.23; H, 4.62.
- (16) Rates were measured by following the magnitude of the symmetric CO stretch of 1 (ca. 2020 cm^{-1}) by infrared spectroscopy. Values of k_1 , k_{-1}/k_2 and k_3 (Table 1) were obtained by fitting the data to curves defined by eq. (2), as shown in Fig. 1.
- (17) Obtained from Aldrich Co. as an approximately 1:1 mixture of the cis and trans isomers.

- (18) A referee has suggested further study of these insertion reactions in a series of solvents having similar nucleophilicities but different polarities. We agree that this would constitute a useful set of experiments, but we are not confident that dielectric constant can be varied systematically without also varying donicity. Merely ascertaining that the coordinating abilities of different solvents toward molybdenum are the same might be difficult, as apparent nucleophilicity often varies with changes in substrate in an unpredictable way (see, for example, Pearson, R. G.; Sobel, H.; Songstad, J. J. Am. Chem. Soc. 1968, 90, 319-326). However; we do not claim to have shown that solvent polarity plays no role in migratory insertion reactions. Our data require only the positive conclusion that coordinative solvent assistance is involved. The examination of a possibly superimposed solvent polarity effect must await the design of more ingenious experiments.
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Table 1. Rate constants^{a,b} for the Reaction of $\text{Cp}(\text{CO})_3\text{Mo}(\text{CH}_3)$ (1) with PMePh_2 at $59.9 \pm 0.01^\circ \text{C}$.

Solvent	$10^4 k_1 (\text{s}^{-1})$	$(k_1/k_2) (\text{M})$	$10^4 k_3 (\text{M}^{-1}\text{s}^{-1})$
THF	7.78 ± 0.07	0.0104 ± 0.0004	1.73 ± 0.08
3-MeTHF	6.46 ± 0.05	0.00821 ± 0.00045	1.86 ± 0.08
2-MeTHF	1.48 ± 0.05	--	1.95 ± 0.12
2,5-Me ₂ THF	0.23 ± 0.03	--	1.67 ± 0.07

^aDefined as shown in Scheme 1; values obtained as described in footnote (16).

^bVariances indicated in table are standard deviations of the derived rate constants. Standard deviation in measured values of k_{obs} is $\pm 1\%$; reproducibility is $\pm 5\%$ or better.

Figure Captions

Fig. 1. Dependence of the pseudo-first order rate constant k_{obs} , for conversion of 1 to 2 in excess PMePh_2 , upon phosphine concentration in the following solvents: ●, THF; ■, 3-MeTHF; ▲, 2-MeTHF; ◆, 2,5-Me₂THF.

Fig. 2. Dependence upon [THF] of k_1 for reaction of 1 with PMePh_2 , determined in studies using 0.01 M 1 and varying excess concentrations of phosphine in THF/2,5-Me₂THF mixtures.

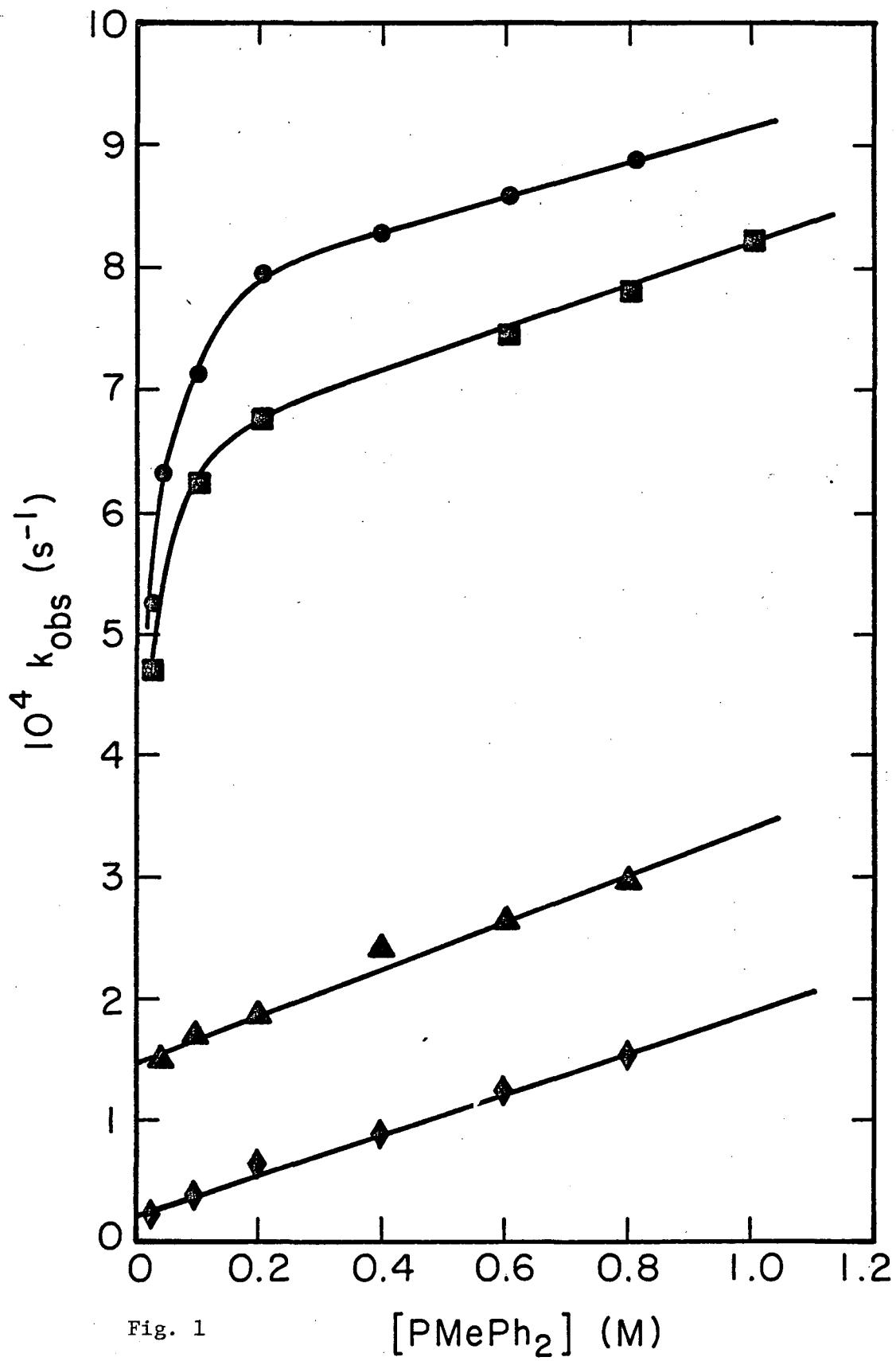


Fig. 1

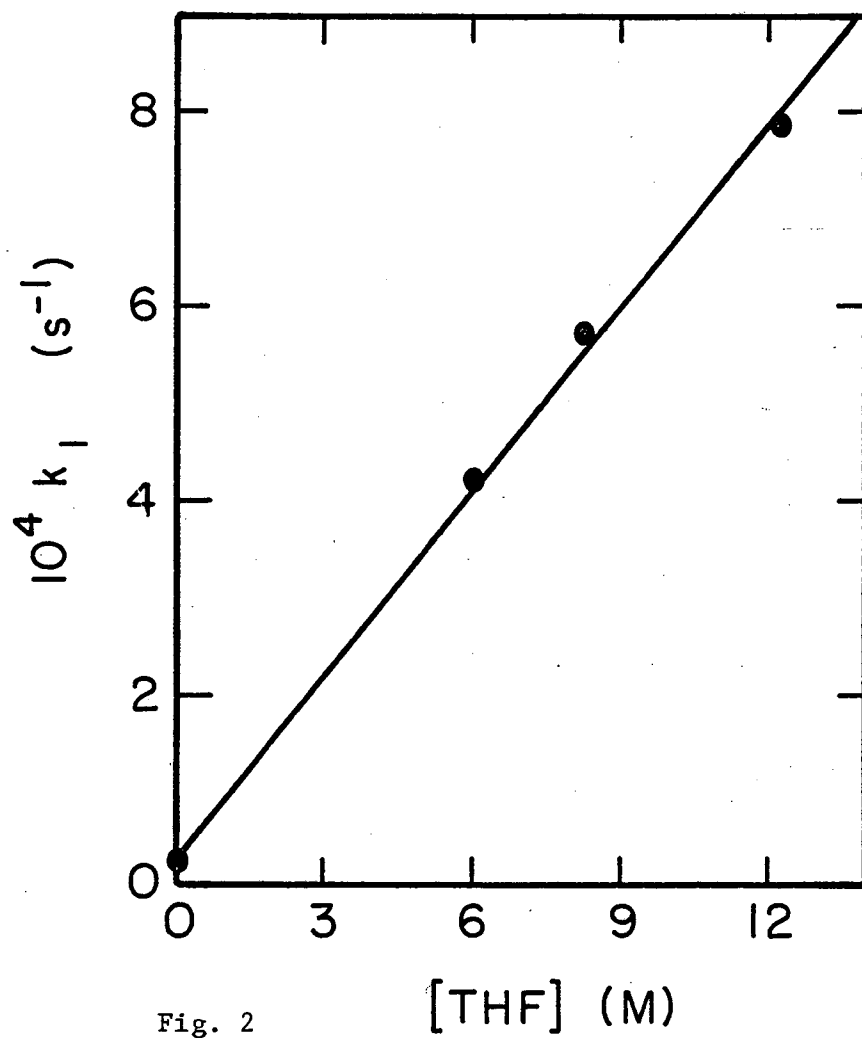


Fig. 2

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