Pressure Acceleration of [2 + 2] Cycloaddition Reactions on the Coordinated Ligand of Chromium and Tungsten Pentacarbonyl Carbene Complexes

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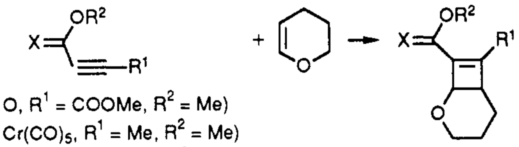
Summary: **The influence of pressure on [2 + 2] cycloaddition reactions of α,β-unsaturated Fischer carbene complexes (M = Cr, W) with 3,4-dihydro-2*H*-pyran was studied. The cycloaddition was found to be sensitive toward pressure and showed a remarkable rate acceleration independent of the metal center. The temperature, pressure, and solvent dependence of these reactions was studied, and the corresponding activation parameters are reported. These data are used to discuss the intimate nature of the cycloaddition process in comparison to related data reported for organic reactions in the literature. The data are consistent with a nonpolar concerted, synchronous one-step mechanism.**

Thermally induced [2 + 2] cycloaddition reactions can only be applied to a limited extent, especially in the reaction of ester-functionalized acetylene derivatives with enol ethers.[2-4] Under drastic experimental conditions, i.e. high reaction temperatures and long reaction times, this reaction can be used to synthesize cyclobutene and its ring-opened products with reasonable yields. If, however, Fischer type alkynylcarbene complexes of Cr and W are used as ester analogues according to the isolobal relationship,[5] such [2 + 2] cycloaddition reactions give moderate to high yields of cyclobutenes under mild experimental conditions according to the overall reaction (1).[6]



(1)

1 (X = O, R¹ = COOMe, R² = Me)
2 (X = Cr(CO)₅, R¹ = Me, R² = Me)
3a (X = W(CO)₅, R¹ = Me , R² = Me)
3b (X = W(CO)₅, R¹ = Ph, R² = Et)

For **1**, a yield of 36% was reported after 16 h at 180 °C in toluene,[3] whereas yields between 82 and 97% were reported for **2** and **3**, respectively, for similar reaction times at room temperature.[6]

It is known from organic chemistry that [2 + 2] cycloaddition reactions are significantly accelerated by pressure with volumes of activation as large as −20 to −55 $\text{cm}^3/\text{mol}^{-1}$.[7-9] In addition, such data have been used to distinguish between the various reaction mechanisms for the cycloaddition process, i.e. a one-step concerted or two-step mechanism. The present investigation was therefore undertaken to study the effect of pressure on such cycloaddition reactions that occur on the coordinated carbene ligand as indicated in reaction 1. A significant acceleration could lead to alternative reaction conditions and possibly induce reactions that do not occur otherwise.[6] A recent study demonstrated that insertion reactions of metal carbene complexes are also significantly accelerated by pressure.[10]

Experimental Section

Materials. The α,β-unsaturated alkynylcarbene complexes (**2**–**3**) were prepared as described in the literature.[11,12] The enol ether 3,4-dihydro-2*H*-pyran (Merck) was distilled and Ar saturated by bubbling Ar through it for at least 15 min. Solutions of the carbene complexes in the neat enol ether were prepared and handled under an Ar atmosphere. Analytical thin-layer chromatography (TLC) was conducted using Kieselgel 60 F 254 (Merck) glass-backed silica gel plates with a 0.2-mm thickness. As chromatography solvent, a mixture of benzene and heptane (1:2) was used.

Instrumentation. UV–vis spectral and kinetic measurements at ambient pressure were performed in the thermostated (± 0.1 °C) cell compartments of Shimadzu UV-250 and UV-2100 spectrophotometers. High-pressure kinetic measurements were performed on a Zeiss DMR 10 spectrophotometer, equipped with a thermostated (±0.1 °C) high-pressure cell.[13] Solutions were placed in a quartz pillbox cell[14] using a special filling technique.[15] This instrument was also used to record UV–vis spectra under pressure (up to 200 MPa).

Kinetic Measurements. The progress of reaction 1 was monitored spectrophotometrically at 455, 435, and 475 nm for **2**, **3a**, and **3b**, respectively. Reactions were followed for at least 3 half-lives, and an infinity absorbance programme was employed to extrapolate the final value. The corresponding pseudo-first-order plots were linear over the studied time range, and the estimated rate constants were reproducible to within 5%.

Results and Discussion

Reaction 1 is accompanied by characteristic changes in the MLCT bands, as indicated in Figure 1 for the investigated systems. The reactions exhibit clean isosbestic points for at least 3 half-lives of the reaction. A similar behavior was observed at elevated pressure, for which the TLC analysis revealed reaction products similar to that found at ambient pressure. Kinetic measurements were performed at wavelengths where maximum absorbance changes occur. The kinetic data are summarized in Table I, and the corresponding activation parameters in Table II. Plots of ln k_{obs} versus pressure were linear within the experimental error limits involved over the investigated pressure range, and $\Delta V^{\ddagger}$ was calculated from the slope

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[1] (a) University of Witten/Herdecke. (b) University of Chicago.
[2] Gollwick, K.; Fries, S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 832.
[3] Nicolaou, K. C.; Hwang, H. C.; Duggan, M. E.; Reddy, K. B. *Tetrahedron Lett.* **1987**, 1501.
[4] Doyle, T. W. *Can. J. Chem.* **1970**, *48*, 1633.
[5] Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725.
[6] Wulff, W. D.; Faron, K. L. *J. Am. Chem. Soc.* **1988**, *110*, 8727.
[7] le Noble, W. J.; Kelm, H. *Angew. Chem.* **1980**, *92*, 887.
[8] Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.
[9] van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.
[10] Schneider, K. J.; Neubrand, A.; van Eldik, R.; Fischer, H. *Organometallics*, in press.
[11] Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229.
[12] Kreissl, F. R.; Fischer, E. O. *J. Organomet. Chem.* **1972**, *35*, C47.
[13] Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
[14] le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976**, *47*, 770.
[15] Wieland, S.; van Eldik, R. *Rev. Sci. Instrum.* **1989**, *60*, 955.

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Table I. k_{obs} as a Function of Temperature and Pressure for Reaction 1[a]

complex	temp, °C	P, MPa	10^5k_{obs},[b] s^{-1}
2	15.0	0.1	6.2 ± 0.2
	25.0		13.3 ± 0.1
	35.0		20.6 ± 0.1
	45.0		57.0 ± 0.4
	25.0	5	14.3 ± 0.5
		50	19.1 ± 0.4
		100	25.4 ± 0.8
3a	15.0	0.1	11.0 ± 0.1
	25.0		21.4 ± 0.2
	35.0		35.9 ± 0.2
	45.0		73.1 ± 0.3
	25.0	5	22.7 ± 0.4
		50	30.9 ± 0.1
		100	40.2 ± 0.1
3b	15.0	0.1	2.3 ± 0.1
	25.0		4.4 ± 0.2
	35.0		8.4 ± 0.5
	45.0		14.9 ± 0.1
	25.0	5	5.0 ± 0.1
		50	6.7 ± 0.1
		100	9.9 ± 0.1

[a] The reactions were studied in neat olefin under conditions similar to those indicated for Figure 1. [b] Mean value of at least three kinetic runs.

Table II. Rate and Activation Parameters for Reaction 1[a]

complex	10^5k_{obs} at 25 °C, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}
2	13.3 ± 0.1	51 ± 3	−147 ± 10	−15.0 ± 0.6
3a	21.4 ± 0.2	45 ± 1	−165 ± 5	−14.9 ± 0.5
3b	4.4 ± 0.2	45 ± 1	−177 ± 3	−17.8 ± 0.5

[a] The quoted activation parameters were calculated from the first-order rate constants in Table I for the reaction in neat olefin.

($=-\Delta V^{\ddagger}/RT$) of such plots in the usual way.[7-9]

The data in Table I clearly demonstrate that the cycloaddition reactions are significantly accelerated by moderate pressures. The corresponding activation volumes are significantly negative and similar for all studied reactions. The reactions are further characterized by large negative $\Delta S^{\ddagger}$ values, which point to a highly structured transition state. The observed pressure effects confirm our expectations that such cycloaddition reactions should exhibit a significant pressure acceleration, since they involve substantial bond formation contributions.

The reported $\Delta V^{\ddagger}$ data can also be used to discuss the intimate nature of the cycloaddition mechanism. For this purpose, it is appropriate to briefly refer to the work that has been performed on [2 + 2] cycloaddition reactions in organic chemistry.[7-9] Typical examples of such reactions include the cycloaddition of tetracyanoethylene and diphenylketene to enol ethers. The former reaction is considered to be a model for [2 + 2] cycloaddition via a zwitterionic intermediate,[16,17] whereas the latter is believed to follow a concerted, but nonsynchronous, mechanism.[18,19] Cycloaddition reactions via a zwitterionic intermediate exhibit significantly negative and strongly solvent-dependent volumes of activation, typically between −19 cm^3 mol^{-1} in MeCN and −46 cm^3 mol^{-1} in CCl_4 for the cycloaddition of tetracyanoethylene to butyl vinyl ether.[20] Of these overal effects −14 cm^3 mol^{-1} was allocated to the intrinsic volume changes and the remainder to solvational effects, i.e. electrostriction. Not only the volumes of activation for such reactions depend on the polarity of the solvent but also the observed rate constants at ambient pressure. In addition such reactions are characterized by strongly solvent-dependent thermal activation parameters, of which $\Delta S^{\ddagger}$ is usually very negative in line with a highly structured transition state.[21]

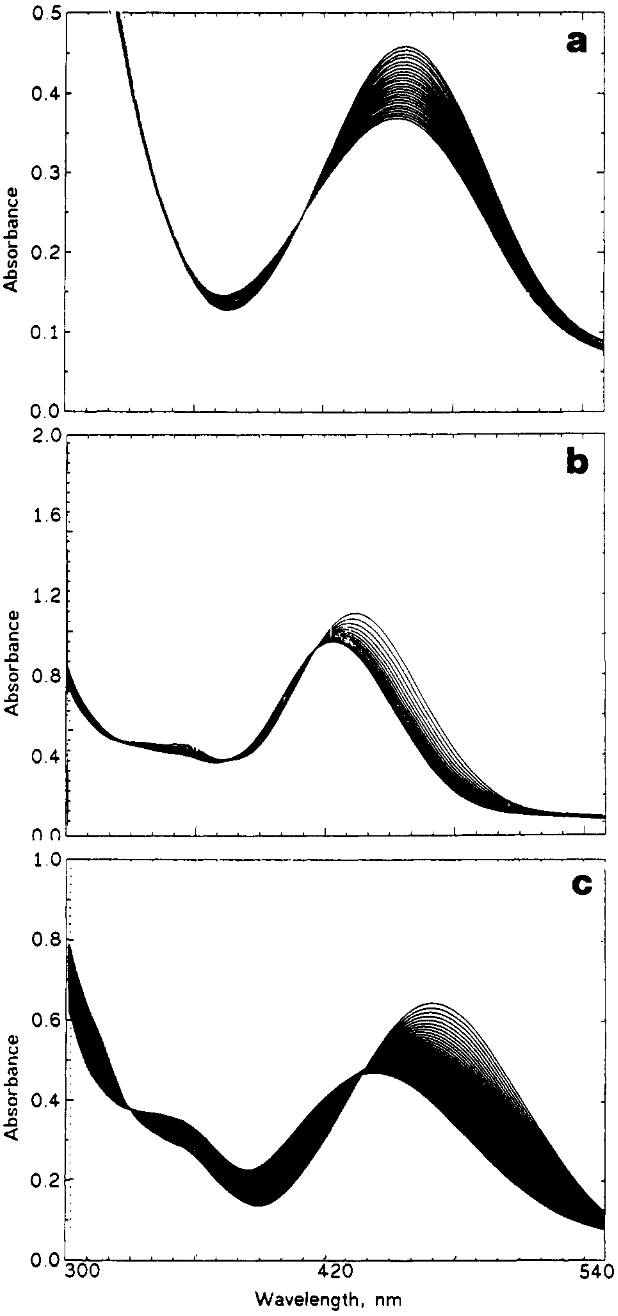

Figure 1. Repetitive scan spectra recorded for the [2 + 2] cycloaddition reactions in 3,4-dihydro-2*H*-pyran. Experimental conditions: [complex] ≈ 7 × 10^{-5} M; T = 25 °C; optical path length = 1.0 cm. Key: (a) **2**; (b) **3a**; (c) **3b**.

For the cycloaddition of diphenylketene to different vinyl ethers, $\Delta V^{\ddagger}$ varies between −22 and −52 cm^3 mol^{-1} and almost equals the overall reaction volume.[19] These reactions do not exhibit such a significant increase in rate constant at ambient pressure with increasing solvent polarity as for the tetracyanoethylene system, which is more

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(16) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

(17) von Jouanne, J.; Kelm, H.; Huisgen, R. *J. Am. Chem. Soc.* **1979**, *101*, 151.

(18) Jenner, G.; Papadopoulos, M. *J. Org. Chem.* **1986**, *51*, 585.

(19) Swieton, G.; von Jouanne, J.; Kelm, H.: Huisgen, R. *J. Chem. Soc., Perkin Trans 2* **1983**, 37.

(20) Fleischmann, F. K.; Kelm, H. *Tetrahedron Lett.* **1973**, *39*, 3773.

(21) Steiner, G.; Huisgen, R. *Tetrahedron Lett.* **1973**, *39*, 3769.

Table III. k_{obs} **as a Function of Solvent for Reaction 1**[a]

				complex 3a			complex 3b		
solvent[b]	ϵ_R	E_T^N	μ, 10^{-30} cm	10^4k_{obs}, s^{-1}	10^4k,[c] M^{-1} s^{-1}	ratio[d]	10^5k_{obs}, s^{-1}	10^5k,[c] M^{-1} s^{-1}	ratio[d]
MeCN	35.9	0.460	11.8	2.61 ± 0.05	0.59 ± 0.01	1.0	5.9 ± 0.3	1.33 ± 0.07	1.0
1,2-$PhCl_2$	9.93	0.225	7.1	3.4 ± 0.1	0.77 ± 0.02	1.30	8.7 ± 0.1	1.97 ± 0.02	1.48
PhMe	2.38	0.099	1.0	2.5 ± 0.1	0.57 ± 0.02	0.97	4.18 ± 0.06	0.95 ± 0.01	0.71
C_7H_{14}	1.92	0.012	0				6.5 ± 0.5	1.47 ± 0.11	1.10
olefin[e]			4.4	7.31 ± 0.03	0.661 ± 0.003	1.12	14.9 ± 0.1	1.35 ± 0.01	1.01

[a] Reactions performed at 45 °C. [b] In all experiments 4.42 M olefin was employed; solvent parameters ϵ_R, E_T^N, and μ were taken from ref 26. [c] Second-order rate constant $k = k_{obs}/[\text{olefin}]$. [d] Relative ratio of rate constants. [e] Olefin = 3,4-dihydro-2*H*-pyrane; 11.06 M in the absence of solvent.

in line with a concerted, nonsynchronous one-step mechanism. The solvent dependence of $\Delta V^{\ddagger}$ is ascribed to the dipolar nature of the transition state. Such reactions are also characterized by significantly negative $\Delta V^{\ddagger}$ values, which point at the ordered nature of the transition state.[22]

In contrast, some [2 + 2] cycloaddition reactions are known that exhibit concerted, nearly synchronous bond formation without significant charge separation in the transition state, for which the observed rate constant is practically independent of solvent polarity.[23-25] Such isopolar transition-state reactions are classed as concerted.

The very similar and small negative $\Delta V^{\ddagger}$ values of ca. -15 cm^3 mol^{-1} found in this study suggest that the cycloaddition process does not involve the formation of either a zwitterionic intermediate or a strongly dipolar transition state. In order to check this statement, some of the reactions were repeated in mixtures of the olefin and various solvents of different polarity, for which the kinetic data are summarized in Table III. The results demonstrate that although the selected solvents cover a large polarity range, the observed rate constants do not exhibit a significant solvent dependence, at most a factor of 2 when the olefin concentration is taken into account. These results underline the operation of an isopolar transition-state reaction, i.e. a concerted mechanism. A further argument supporting this mechanism is that changing the methyl substituent for phenyl has no marked effect on the observed rate constants. This is typical for pericyclic reactions that proceed according to a concerted mechanism.[26] Some experiments were also performed in MeOH as solvent, since zwitterionic intermediates can be intercepted with alcohols.[27,28] The carbene complexes, however, reacted relatively fast with MeOH in the absence of added olefin, which complicated the interpretation of the observed spectral changes.

Our $\Delta V^{\ddagger}$ values are remarkably close to the intrinsic contribution of -14 cm^3 mol^{-1} estimated from the solvent-dependence data for the cycloaddition of tetracyanoethylene to butyl vinyl ether that occurs via a zwitterionic intermediate.[20] Nonetheless, the absence of significant solvent effects and the relatively small absolute value of $\Delta V^{\ddagger}$ demonstrate that we are mainly observing intrinsic volume effects associated with bond formation during the formation of a nearly isopolar transition state. A similar conclusion was reached for the cycloaddition of tetracyanoethene to tricarbonyl(cycloheptatrienone)iron, for which $\Delta V^{\ddagger}$ was also found to be independent of the nature of the solvent.[29] The fact that an isopolar transition state is formed during the auxiliary cycloaddition reactions must be related to the role of the pentacarbonylmetal carbene moiety attached to the alkynyl group undergoing the cycloaddition reaction. This could be explained in terms of effective back-bonding and delocalization of electron density on the $(O{\equiv}C)_5M{=}C{-}C{\equiv}C$ moiety. The isopolar nature of the transition state suggested to account for the rate and activation parameters reported in this study does not have to occur for all auxiliary [2 + 2] cycloaddition reactions. For instance, the introduction of a $SiMe_3$ substituent has been suggested to stabilize a zwitterionic intermediate.[30] In this case, the corresponding rate and activation parameters should exhibit a significant solvent dependence.

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Registry No. **2**, 92314-85-7; **3a**, 103225-99-6; **3b**, 36009-08-2; 3,4-dihydro-2*H*-pyran, 110-87-2.

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(22) Brady, W. T.; O'Neal, H. R. *J. Org. Chem.* **1967**, *32*, 612.

(23) Baldwin, J. E.; Kapeck, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4868.

(24) Schaumann, E. *Chem. Ber.* **1976**, *109*, 906.

(25) Dondoni, A.; Battaglia, A.; Bernardi, F.; Giorgianni, P. *J. Org. Chem.* **1980**, *45*, 3773.

(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, Germany, 1988.

(27) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.

(28) Huisgen, R.; Schug, R.; Steiner, G. *Angew. Chem.* **1974**, *86*, 47.

(29) Hallinan, N.; McArdle, P.; Burgess, J.; Guardado, P. *J. Organomet. Chem.* **1987**, *333*, 77.

(30) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419.