COMMENTS

"Phantom Activation Volumes" Are Indeed Real Activation Volumes

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Introduction

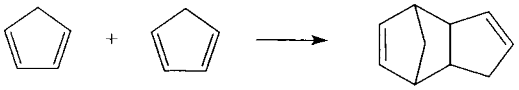
It is well-known from the literature that the volume of activation, $\Delta V^{\neq}$, for a chemical reaction in solution is an important parameter in the assignment of intimate reaction mechanisms in all areas of solution phase chemistry.[1−3] Although much of the original work in this area was performed by physical-organic chemists, later work, especially the development of suitable instrumentation to study the kinetics of fast reactions at high pressure, was performed by physical-inorganic chemists. The volume of activation is determined from the pressure dependence of the reaction rate constant as defined in eq 1 and. in terms of the transition-state theory. represents the change in partial molar volume in going from the reactant to the transition state of a particular reaction:

$$\frac{\mathrm{d}\ln k}{\mathrm{d}P} = -\frac{\Delta V^{\neq}}{R\cdot T} \qquad (1)$$

Typical cycloaddition reactions in organic chemistry are characterized by large negative volumes of activation; i.e., they show a significant acceleration on increasing pressure, as a result of bond formation and solvent contraction in the transition state. Diels−Alder reactions, for example, are significantly accelerated by pressure, and the corresponding $\Delta V^{\neq}$ values range from −25 to −50 cm^3 mol^{-1}.[4]

Workers in this area were recently astonished by a paper published by Swiss and Firestone on "Phantom Activation Volumes".[5] In this study, the authors claim that volumes of activation determined from the effect of pressure on the rate constant of a chemical reaction are only partially volume derived since increasing pressure can induce other kinetic effects that do not arise from volume changes. These authors therefore propose the term phantom activation volumes (PAV) for pressure-induced changes in rate constants that are not volume related. Two possible sources for PAV were mentioned, viz. changes in solvent polarity and changes in solvent viscosity. The first effect (electrostriction) is a real volume effect which is well understood by workers in this field since the polarity of a solvent may change as a function of pressure and thus accelerate or decelerate a chemical reaction that is sensitive to solvent polarity. The second source is known to play a role in diffusion-controlled processes where transition-state theory fails, since solvent viscosity increases with pressure and in turn retards such a reaction. However, the authors claim that pressure-induced solvent viscosity increases can also accelerate the rate constants of (for instance) Diels−Alder reactions where transition-state theory applies, based on earlier data published by these authors.[6] How illogical it may sound, the authors did report an increase in the rate of two cycloaddition reactions upon increasing the solvent viscosity, of which the Diels−Alder dimerization of cyclopentadiene showed the largest viscosity dependence.[6] If this is generally true as claimed by the authors, it would cause an increase in rate constant on increasing pressure not related to volume changes and therefore defined as PAV. The authors[5] then went one step further and "corrected" numerous activation volume data reported in the literature for Diels−Alder cycloaddition reactions for the contribution from PAV, to obtain a corrected volume of activation on which basis mechanistic conclusions should now be drawn. Predictably, this paper[5] immediately drew the attention of well-established workers in this field, and two of them disputed the validity of the PAV approach in the literature.[7,8]

We decided to re-examine the claim made by the authors[6] that a cycloaddition reaction can indeed be accelerated by solvent viscosity, which in our view is the basis of this fundamental disagreement. Swiss and Firestone[6] studied the dimerization kinetics of cyclopentadiene (reaction 2) and found that as the solvent viscosity rises from 0.5 to 1.5 (cP), the second-order rate constant increases by a factor of ca. 2.5. This reaction showed the largest viscosity effect of the three systems studied; the increase in rate was suggested to be viscosity-induced.[6]


(2)

The authors argued that the published negative activation volumes for Diels−Alder reactions in *n*-alkane solvents are partially "non-volume-related" and must be treated as PAV.[5,6] Thus, for the dimerization of cyclopentadiene, 61% of the experimental activation volume should be non-volume-related and merely 39% is in fact "volume-related" on the basis of their data. A careful analysis of the rate data (supplied as Supporting Information)[6] on which their conclusion was based reveals that the authors followed reaction 2 in the following *n*-alkanes (the overall conversion is indicated in brackets): *n*-octane (18%), *n*-decane (10%), *n*-undecane (15%), *n*-dodecane (22%), *n*-tridecane (21%), *n*-tetradecane (17%), and *n*-heptadecane (45%). The very low conversions could possibly lead to large error limits in the reported rate constants. For this reason, we have repeated these kinetic measurements over reaction periods of at least one half-life of the reaction, which in some cases took as long as 70 days at 30 °C. The results reported here clearly show that reaction 2 shows no viscosity dependence at all, and we conclude that the claimed PAV's are in fact real activation volumes.

Experimental Section

All chemicals used were of analytical reagent-grade and purchased from Merck. Cyclopentadiene was prepared freshly

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each time via dissociation of the dimer at its boiling point and appropriate distillation.[9] Approximately 0.2 mL cyclopentadiene was diluted to a volume of 25 mL with the hydrocarbon solvents *n*-octane, *n*-decane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-heptadecane. The reaction flasks containing these solutions were fitted with screw-cap tops. This served two purposes: to prevent the loss of solvent through evaporation and the entrance of water during the long reaction periods. These solutions were placed in a thermostated water bath at 30 °C with constant sample shaking. Aliquots (0.15 mL) of the reaction solutions were removed every 3−4 days and diluted to a volume of 25 mL with HPLC-grade *n*-hexane. The concentration of cyclopentadiene in the diluted aliquots was determined by UV−vis spectrophotometry ($\lambda_{\max} = 240$ nm, $\epsilon = 3390$ M^{-1} cm^{-1}).[10] The kinetic measurements were continued until at least 50% conversion was achieved, which required measurements for periods from 7 to 10 weeks.

UV−vis measurements were performed on a Cary 1 spectrophotometer with a 1 cm quartz cuvette. NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer. Mass spectra were obtained on a JEOL M Station 700 mass spectrometer applying the FD technique.

Results and Discussion

The main objective of this study was to determine whether viscosity has an effect on the Diels−Alder dimerization of cyclopentadiene (reaction 2), and for this reason, a series of *n*-alkane solvents of varying viscosity was selected. For each solvent, the disappearance of the monomer was followed by UV−vis spectroscopy, and the products formed were monitored by NMR spectroscopy. During the course of the study, two experimental difficulties were encountered. First, the dimerization reaction is slow and has to be followed over extremely long reaction times at a temperature of 30 °C. An attempt to study the reaction at 40 or 50 °C was unsuccessful since the reverse reaction becomes significant and the system reaches an early equilibrium. Reaction 2 is an exothermic process such that the retro Diels−Alder reaction is preferred at higher temperatures, i.e., the technique employed to prepare fresh samples of the monomer. Second, in some cases, solubility problems occurred either at the start of the reaction or during the reaction related to either the solubility of the monomer or the solubility of the dimer in various *n*-alkane solvents, respectively. This was observed as a slight cloudiness of the solutions. In an effort to overcome the solubility problems at the start of the reaction, we added 1-chlorobutane (10 vol. %) to the solvent since it has been reported to be suitable for the studied reaction.[11] For each solvent, four sample solutions were prepared: two with and two without 10% 1-chlorobutane. Unfortunately, the addition of 1-chlorobutane did not always have the expected effect. The occurrence of cloudiness in a particular reaction is indicated in the reported data. Kinetic measurements were carried out on all four sample solutions for each selected solvent.

Under the selected conditions, the dimerization reaction of cyclopentadiene (Cp) to dicyclopentadiene is a second-order process for which the rate law is given in eq 3. According to this equation, plots of $1/[\mathrm{Cp}]_t$ versus reaction time (t) should be linear with a slope of $2k_2$, where k_2 is the second-order rate constant for reaction 2:

$$1/[\mathrm{Cp}]_t - 1/[\mathrm{Cp}]_o = 2k_2t \qquad (3)$$

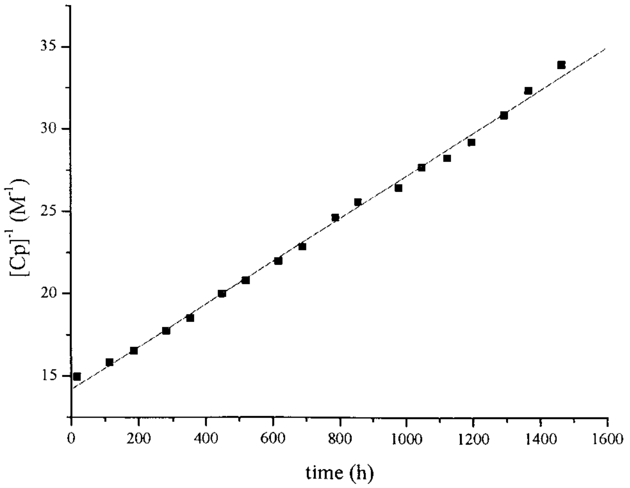

Figure 1. $[\mathrm{Cp}]^{-1}$ vs reaction time for the dimerization of cyclopentadiene in *n*-tridecane at 30 °C. The measurement was performed until 56% conversion was achieved.

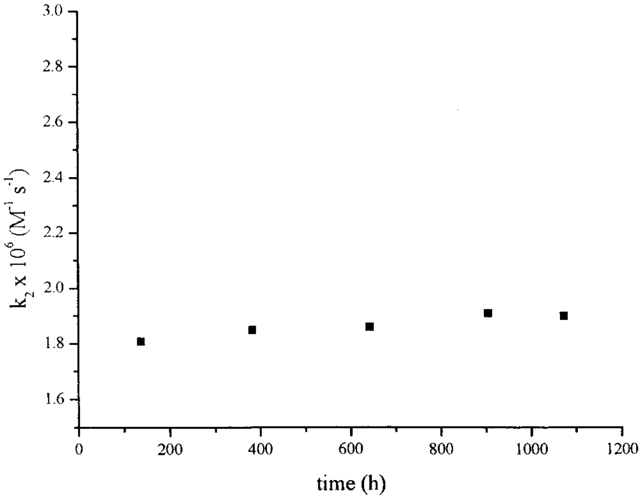

Figure 2. k_2 vs reaction time for the dimerization of cyclopentadiene in *n*-heptadecane at 30 °C.

Figure 1 presents a typical plot of $1/[\mathrm{Cp}]_t$ versus time for the dimerization of cyclopentadiene in *n*-tridecane at 30 °C. The measurements were continued until 56% conversion of the starting material was achieved. The plot in Figure 1 shows good linearity, and this is representative of all the kinetic plots obtained for the various solvents used in the absence of 1-chlorobutane. In some cases, the second-order plots seem to suggest an increase in rate constant with time. To check the influence of conversion on the rate constant, we calculated the slope of the plot as a function of reaction time. Two typical examples are shown in Figures 2 and 3 for the reaction in *n*-heptadecane and *n*-decane, respectively, where clear solutions were observed under all conditions. In Figure 2, the value of k_2 remains practically constant during the reaction. In Figure 3, the second-order rate constant seems to increase somewhat with increasing reaction time and reaches an almost constant value after ca. 600 h. In this case, a cloudy solution was observed at the start of the reaction which became clear after 7−10 days. This is apparently related to the limited solubility of cyclopentadiene in *n*-decane. The addition of 10 % (vol.) of 1-chlorobutane to *n*-decane resulted in a permanently cloudy solution. The corresponding plot of k_2 versus reaction time given in Figure 4 shows a strong increase in the rate constant with increasing time, apparently caused by the cloudiness of the solution.

Table 1 summarizes the experimentally determined rate constants for the dimerization of cyclopentadiene at 30 °C in

TABLE 1: Values of the Second-Order Rate Constant 10^6 k_2 (M^{-1} s^{-1}) at 30 °C for the Dimerization of Cyclopentadiene in Different *n*-alkane Solvents

solvent	viscosity (25 °C, cP)	without addition of 1-chlorobutane I	II	with addition of 10% (vol) 1-chlorobutane I	II
n-octane	0.509	1.59 ± 0.03	1.64 ± 0.04	2.14[a] ± 0.07	2.13[a] ± 0.17
n-decane	0.832	1.56 ± 0.03	1.53 ± 0.01	2.25[a] ± 0.06	2.22[a] ± 0.07
n-dodecane	1.32	2.31[a] ± 0.04	2.42[a] ± 0.04	2.75[a] ± 0.10	2.63[a] ± 0.10
n-tridecane	1.612	1.81 ± 0.03	1.78 ± 0.03	1.64 ± 0.03	1.67 ± 0.04
n-tetradecane	1.998	2.64[a] ± 0.04	2.66[a] ± 0.06	2.67[a] ± 0.04	2.60[a] ± 0.06
n-heptadecane	3.41	1.90 ± 0.02	1.95 ± 0.03	1.82 ± 0.04	1.78 ± 0.04

[a] Solutions that turned cloudy during the reaction, see text.

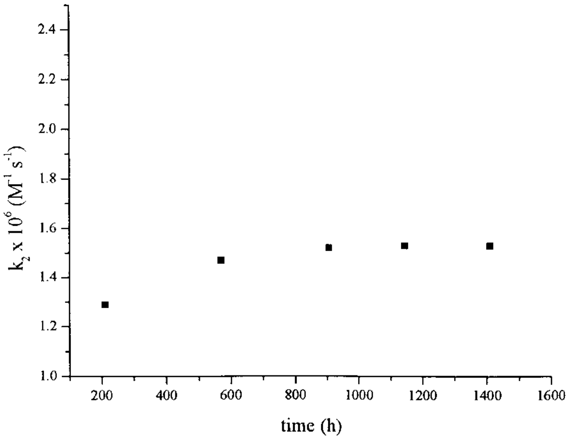

Figure 3. k_2 vs reaction time for the dimerization of cyclopentadiene in *n*-decane at 30 °C. Cloudiness of the solution was observed at the start of the reaction, which cleared during the course of the reaction.

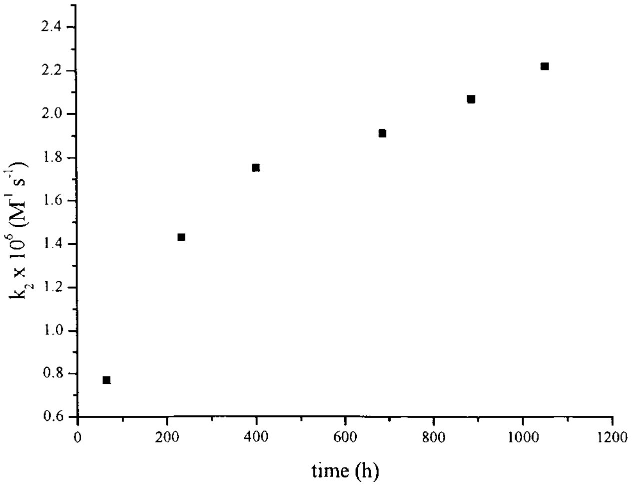

Figure 4. k_2 vs reaction time for the dimerization of cyclopentadiene dimerization in *n*-decane with 10 vol % 1-chlorobutane at 30 °C. The reaction solution was cloudy throughout the reaction.

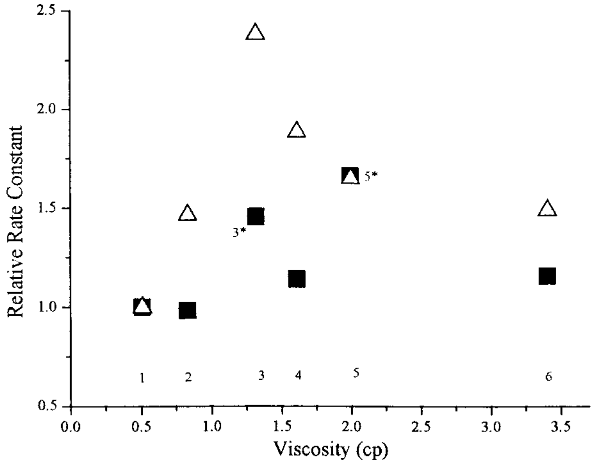

Figure 5. Relative rate constant vs viscosity for the dimerization of cyclopentadiene at 30 °C in the following solvents: (1) *n*-octane; (2) *n*-decane; (3) *n*-dodecane; (4) *n*-tridecane; (5) *n*-tetradecane; (6) *n*-heptadecane. (■) Relative rate constants determined in this study at 30 °C; (△) relative rate constants detemined by Swiss and Firestone at 25 °C.[6] The points labeled with an asterisk are those obtained from reaction mixtures that turned cloudy during the reaction.

all selected solvents. Each series of experiments was repeated twice (indicated by I and II), and the rate constants quoted are the mean values of at least two determinations in each series. In this way, more than 50 kinetic experiments were performed. The reproducibility was rather good, with error limits between 1% and 8%. By way of comparison, Swiss and Firestone[6] reported a rate constant of 0.76 × 10^{-6} M^{-1} s^{-1} in *n*-octane and 1.26 × 10^{-6} M^{-1} s^{-1} in *n*-tetradecane for the dimerization reaction at 25 °C, which is in good agreement with our findings if the 5 °C higher temperature is taken into account. However, in the case of *n*-decane, *n*-dodecane, *n*-tridecane, and *n*-heptadecane as the solvent, the authors[6] reported rate constants of 1.12 × 10^{-6}, 1.82 × 10^{-6}, 1.44 × 10^{-6}, and 1.14 × 10^{-6} M^{-1} s^{-1}, respectively, which are substantially higher than those found in the present study if the temperature difference of 5 °C is taken into account. According to the data in Table 1, the rate constants for the reactions in clear solutions at 30 °C are all below 2 × 10^{-6} M^{-1} s^{-1}, whereas those for cloudy solutions are all above 2 × 10^{-6} M^{-1} s^{-1}. The latter is partly due to the observed increase in rate constant during the reaction as shown in Figures 3 and 4. The relative rate constants are plotted as a function of viscosity in Figure 5 and compared to those reported before.[6] Viscosity data were taken from the literature.[6] A comparison of the rate constants measured for the clear solutions (points 1, 2, 4 and 6) demonstrates that there is no significant increase in the rate constant for the dimerization of cyclopentadiene with increasing viscosity. Points 3 and 5 are experimental points for solutions that turned cloudy during the reaction and clearly do not fit the correlation. Even if these rate constants would be correct, the apparent viscosity-induced acceleration of the reaction will then be a factor of 1.5 as compared to a factor of 2.5 reported by the previous investigators.[6]

Our observation that cloudy solutions result in higher rate constants could have several causes. One possibility is that the formation of cloudiness during the reaction, i.e., the formation of less soluble products, could cause adsorption of reactant molecules on the surface of the precipitate and hence an extra decay component in the reactant concentration and thus too high a rate constant measured on the basis of the disappearance of the reactant. This would account for the significant increase in rate constant with reaction time (accompanied by the appearance of cloudiness) as shown in Figure 4. The occurrence of cloudiness at the initial stage of the reaction (due to the limited solubility of the reactant in a particular solvent) also causes an

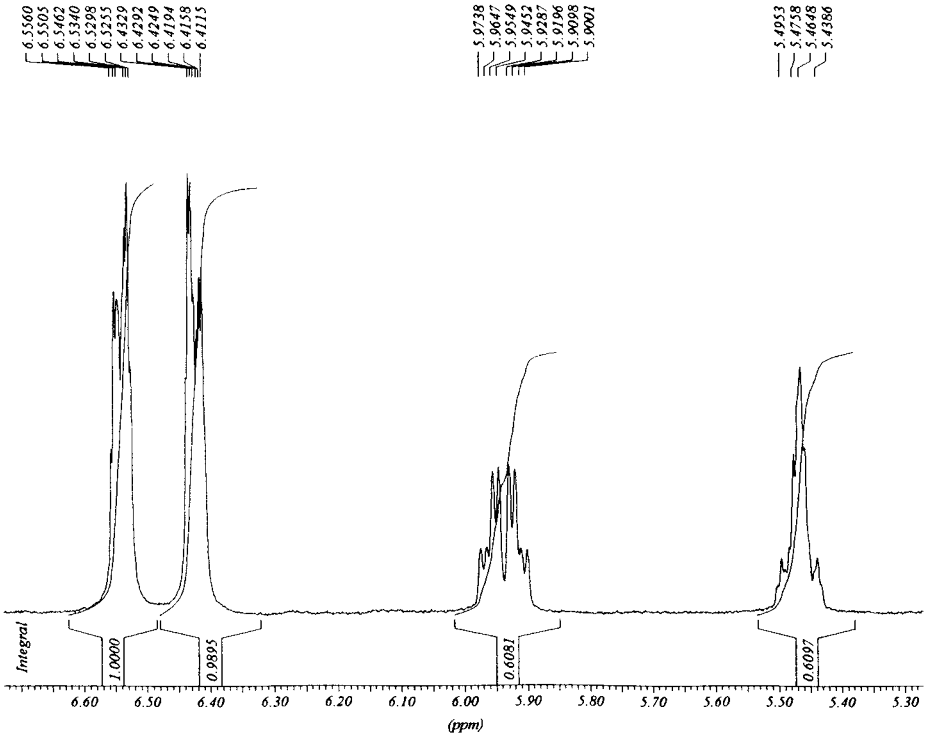

Figure 6. Section of ^{1}H NMR spectrum for the dimerization of cyclopentadiene in *n*-octane as solvent at 58% conversion (clear solution).

increase in the rate constant with increasing reaction time as seen in Figure 3, but the maximum rate constant does not exceed that observed for clear solutions. In the case where cloudy solutions formed during the reaction, the formation of a yellow, jelly-like precipitate was observed over longer reaction times. Mass spectrometric analyses suggest that the yellow precipitate is a polymeric species, with signals for its decomposition products at m/z 279 and 390 in the mass spectrum. This material is presumably formed during the polymerization of the dimer with further monomers.[12] This would also result in a more rapid decrease in the concentration of the monomeric species, i.e., an increase in the second-order rate constant for the disappearance of the reactant at longer reaction times.

A section of the ^{1}H NMR spectrum (300 MHz) of the reaction mixture obtained during the dimerization of cyclopentadiene in *n*-octane (clear solution) at 58% conversion is shown in Figure 6. The conversion was determined by UV−vis spectroscopy. The peaks in the ^{1}H NMR at 6.4 and 6.5 ppm are assigned to the cyclopentadiene reactant.[13] The peaks at 5.4 and 5.9 ppm are assigned to the cyclopentadiene dimer product. As the reaction proceeds, the relative intensity of the resonances due to the dimer product increases, and those due to the monomer decrease. During the course of the reaction, no side products could be detected in the NMR spectra. All in all, only reactant, product, and solvent signals were observed. This was the case in all solvents, with the only difference that the overall conversion based on the UV−vis spectra and those observed in the NMR spectra deviated significantly in the case where cloudiness occurred and a precipitate was formed. In those cases, the conversion observed in the NMR spectra was too low since a portion of the product had precipitated.

Conclusions

For the Diels−Alder dimerization of cyclopentadiene in various hydrocarbon solvents of different viscosities, the second-order rate constants show essentially no dependence on viscosity under conditions in which the solutions remained clear throughout the reaction. This is in accordance with claims in the literature that the rate of Diels−Alder reactions is not strongly influenced by variation of the solvent[14] and the fact that there is no obvious reason this reaction should exhibit a viscosity dependence at all. In the case of *n*-dodecane and *n*-tetradecane as the solvent, there are solubility problems; on the whole, we can conclude that cloudy solutions show higher rate constants than those observed for clear solutions. There is no indication from our data that a part of the experimental activation volume for the Diels−Alder dimerization of cyclopentadiene in the studied viscosity range is not volume related. The apparent discrepancy between the data reported here and that reported by Swiss and Firestone[6] is most probably related to the problems encountered with cloudiness in some solvents and the fact that the authors[6] studied the reactions to much lower conversions, i.e., for much shorter reaction times. We conclude that there is no viscosity-induced acceleration of the investigated Diels−Alder reaction. Even if there was an appreciable effect, no reasonable mechanism would account for it. Thus, there is no need to postulate phantom activation volumes, as done by Swiss and Firestone,[5] in the absence of convincing experimental evidence.

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Supporting Information Available: Representative plots of $[\mathrm{Cp}]^{-1}$ versus reaction time for the dimerization of cyclopentadiene in all solvents studied (6 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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