a solution of α-methylstyrene (1.7 mmol) in methanol (10 mL) was added and the reaction was continued with stirring at 6–8 °C for 3 h. α-Methylstyrene oxide (**29**) and acetophenone (**8**) were isolated quantitatively by column chromatography on silica gel.

Treatment of α-methylstyrene with oxone in aqueous methanol in the absence of acetophenone, however, resulted in the recovery of α-methylstyrene.

Ozonolysis of 1-Methyl-2-methoxystyrene in the Presence of α-Methylstyrene. The reaction of a mixture of **3b** (2 mmol) and α-methylstyrene (**28**, 2 mmol) with an ozone molecule in carbon tetrachloride was undertaken at 0 °C. The products were separated by column chromatography on silica gel. From the first fraction **28** was recovered quantitatively. The second fraction contained tetroxane **7** (30% yield). From the final fraction acetophenone (**8**) was obtained in 21% yield.

Acknowledgment. We thank Dr. Kevin J. McCullough of Heriot-Watt University and Prof. Karl Griesbaum of Universität Karlsruhe for useful discussions.

Volumes of Activation for the Cycloaddition Reactions of Phenylhalocarbenes to Alkenes

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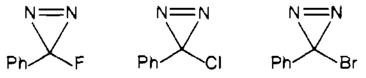
Abstract: The absolute rate constants for the cycloaddition reactions of three arylhalocarbenes to two alkenes have been measured as a function of pressure in the range 0.1 to 203 MPa. In all cases the observed rate constants were found to increase with increasing pressure. The magnitude of the derived activation volumes falls in the range of −10 to −18 cm^3/mol and does not depend on solvent. The results rule out a late, two-bond transition state and a bipolar single-bond transition state but are consistent with the reversible formation of a carbene–alkene complex or an early one- or two-bond transition state.

A considerable literature concerned with the effect of pressure on chemical reactions in solution has been developed over the past two decades.[1] Although the bulk of this literature is concerned with thermal reactions, an increasing number of reports concerned with the influence of pressure on photophysical processes in solution have recently begun to appear;[2,3] however, reports of the influence of high pressure on organic photoreactions in solution are scarce.[4] The few published examples include the effect of pressure on the product ratios in type II photoreactions,[5] on the product distributions in photocycloadditions to naphthalene,[6] and on the photoreduction of benzophenone.[7] To date, there have been no reports in the literature concerning the influence of pressure on the absolute rate constants of photoinduced cycloaddition reactions.[8]

We report here the results of an investigation of the influence of pressure in the range 0.1–203 MPa on the absolute rate constants for the additions of phenylhalocarbenes to alkenes. Many absolute rate constants for these reactions have been measured at 0.1 MPa (atmospheric pressure).[9a] The results of variable temperature experiments have demonstrated that negative temperature coefficients (faster rates at lower temperatures) are characteristic of the most rapid of these reactions.[9b] Arrhenius analysis of the data demonstrates that entropy factors are of critical importance in determining the absolute rate constants.[9] The factors that determine the effect of pressure on rate constants are often similar to those that determine entropy changes (i.e., the transition state has fewer degrees of freedom than the initial state),[1,10] so that it is of particular current interest to measure the influence of pressure on the magnitude of the absolute rate constants for the additions of phenylhalocarbenes to alkenes.

Experimental Section

Chart I



1 2 3

Phenylfluorodiazirine (**1**), phenylchlorodiazirine (**2**), and phenylbromodiazirine (**3**) were synthesized and purified as described previously (Chart I).[11] Tetramethylethylene (TME; Aldrich) and *trans*-2-pentene (TP; Aldrich) were distilled immediately before use. Spectroscopic grade methylcyclohexane (MCH; Aldrich) was used without further purification. The samples were not degassed. The laser flash photolysis apparatus was similar to that described in the literature.[12a] The high-pressure cell and the associated techniques were described previously.[12b] Transient absorption experiments were performed by employing the third harmonic (355 nm) of a Quanta Ray Nd:YAG laser, pulse width ca. 10 ns. A 150-W xenon lamp, together with a PRA 301 power supply and a PRS

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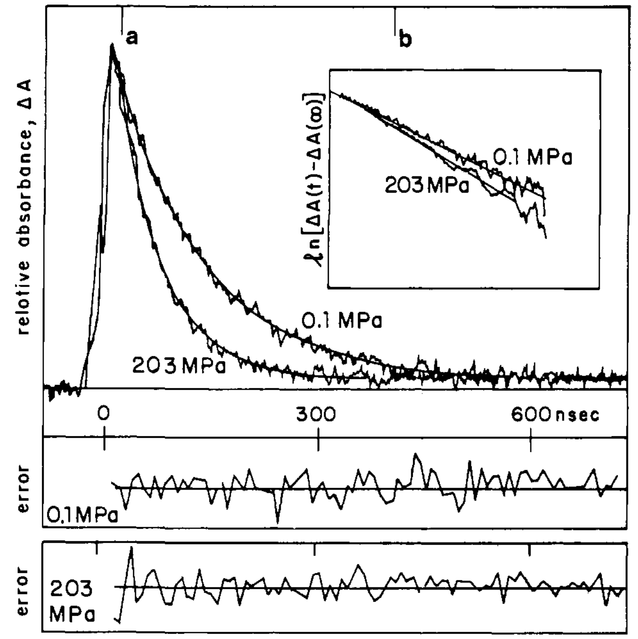

Figure 1. Typical decay curves for the PhCCl–TME–MCH system at pressures of 203 and 0.1 MPa. [TME] = 0.020 M at 0.1 MPa. The ordinate shows the absorbance of PhCCl in arbitrary units; time (ns) is depicted on the abscissa. The insert presents the data in logarithmic form for the decay between points a and b (top of figure).

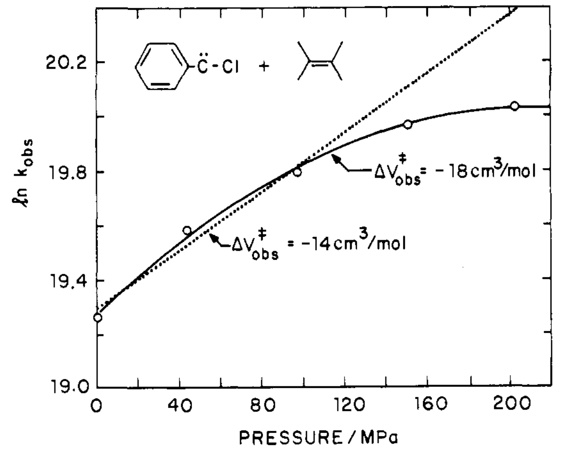

Figure 2. Plot of ln k_{obsd} against pressure for the PhCCl–TME–MCH system. The solid line shows a correlation obtained by quadratic analysis.[14,17b] The dotted line shows a least-squares linear plot of the initial three points.

305 pulse unit, was employed as the analyzing light source. The transmitted analyzing light intensities were monitored by using six dynodes of a RCA 4840 photomultiplier tube, the output of which was passed through an automatic backoff box, and terminated with a 93 ohm resistor and digitized with a Tektronix 7912 AD device. All data were analyzed on a PDP 11/23 computer which was interfaced to the digitizer. The concentrations of the diazirines were adjusted so that the solutions had absorbances of ca. 0.8 at 355 nm. The change in the concentrations of the alkenes with increasing pressure was corrected by taking account of the known compressibility of MCH.[13]

Results

Three carbenes [PhCF, PhCCl, PhCBr] that have been extensively investigated in our laboratories[9] were examined with tetramethylethylene and *trans*-2-pentene as substrates. The carbenes were generated by photolysis of diazirines **1**–**3**. The reactions of the carbenes with these alkenes are known to afford the anticipated cyclopropane products.[9] A typical example of the influence of pressure on the pseudo-first-order decay of the carbenes is shown in Figure 1 by using the reaction of PhCCl and TME as an example. The rate constants for the carbene reactions as a function of pressure were evaluated from observations such as those shown in Figure 1 by conventional methods,[9] i.e., the bimolecular rate constants, k_{obsd}, for the carbene reactions were evaluated from the plots of pseudo-first-order rate constants for decay against alkene concentration. Plots of the logarithms of the observed rate constants as a function of pressure were of two types: for the faster reacting carbenes, the plots were decidedly curved throughout the pressure range (Figure 2), whereas for the slower reacting carbenes the correlations were linear throughout the pressure range investigated (Figure 3). The activation volumes for the carbene additions were evaluated from the initial, linear portions of the rate constant/pressure profiles and are listed in Table I. For comparison, the activation volumes evaluated from a standard quadratic fitting procedure[14] are also listed in Table I.

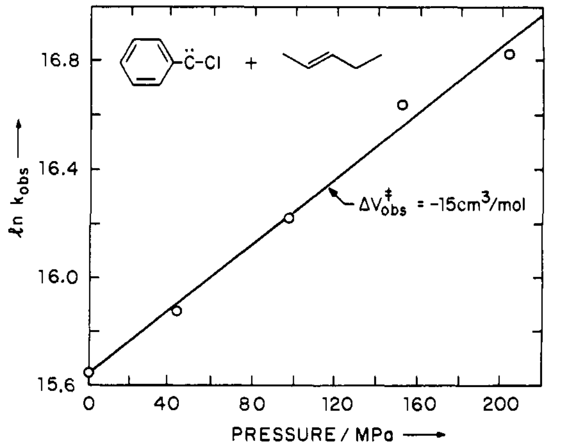

Figure 3. Plot of ln k_{obsd} against pressure for the PhCCl–TP–MCH system.

Table I. Volumes of Activation $\Delta V^{\ddagger}_{\mathrm{obsd}}$ (cm^3/mol) for the Additions of Carbenes to Alkenes in MCH and Acetonitrile[a]

	PhCF	PhCCl	PhCBr
MCH solvent			
TME	−17 ± 3 (−22 ± 4)	−14 ± 3 (−18 ± 2)	−10 ± 1 (−13 ± 3)
trans-2-pentene	−18 ± 2	−15 ± 1	−12 ± 1
CH_3CN solvent			
TME		−14 ± 1	
trans-2-pentene		−14 ± 1	

[a] The numbers in parentheses are the volumes of activation obtained by a quadratic analysis of the data. See ref 17b for the details of this analysis.

Table II. Values of k_{-1}/k_2 (Based on the Assumption of a Reversibly Formed Complex) for the Additions of Phenylhalocarbenes to TME in MCH

pressure[a]	PhCF	PhCCl	PhCBr
0.1	64	41	27
44	26	18	14
97	12	9.0	6.8
151	7.1	4.3	4.0
203	3.9	2.4	2.3

[a] Pressure units MPa.

Discussion

The volume of activation for the rate-determining step of a reaction sequence may be evaluated from the pressure dependence of the rate constant of the reaction. The "experimentally observed" activation volume ($\Delta V_{\mathrm{obsd}}^{\ddagger}$) is generally thought to consist of an

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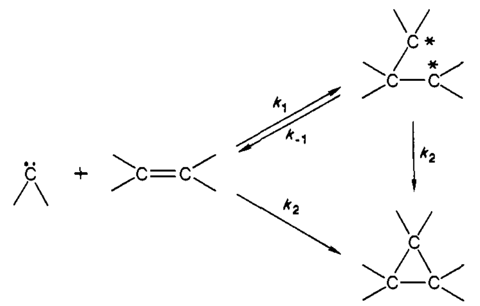
Scheme I



intrinsic term ($\Delta V_{int}^{\ddagger}$) and a solvent term ($\Delta V_{sol}^{\ddagger}$).[1,4] The intrinsic term results from the formation and cleavage of bonds in the rate-determining transition state, whereas the solvent term reflects the change in polarity of the species involved in the rate-determining transition state.[1,4] Of course, the separation of these terms may not be straightforward and, in addition, the assumption that the measured rate constant refers to a single, rate-determining step may not be valid. However, such ambiguities are characteristic of nearly all kinetic analyses. The study of rate constants as a function of pressure nevertheless merits attention because the volume parameters thus determined possess considerable intuitive appeal and assist us in characterizing the reaction mechanism.

In the case of cycloaddition reactions, we envision three limiting mechanisms. In two of the mechanisms a reversibly formed complex (either a biradical or a zwitterion) is involved, and in the third mechanism a single concerted step is involved. The biradical mechanism which involves a loosely formed complex with a biradicaloid intermediate or complex, should result in a moderately negative volume of activation and a negligible solvent polarity effect. On the other hand, the zwitterion mechanism, which involves a loosely formed complex with a charge-separated intermediate, should result in a moderately negative volume of activation and a significant solvent polarity effect. The concerted mechanism should result in a relatively large negative volume of activation, with a negligible solvent polarity effect. Thus, an investigation of the influence of pressure on the kinetics of cycloaddition, combined with a determination of solvent effects, affords in principle a means of differentiating between the three mechanisms.

The additions of phenylhalocarbenes to alkenes are accelerated by the application of modest pressure (ca. 100 MPa). For example, in the case of phenylchlorocarbene and TME the rate constant doubles upon increasing the pressure from 0.1 to 100 MPa. Thus, it is clear that the $\Delta V^{\ddagger}$ are all negative. From Table I we see that the activation volumes are all in the range of -10 to -18 cm^3/mol.

Additions of phenylhalocarbenes to alkenes have been analyzed in terms of (1) the formation of a carbene/alkene complex that can either dissociate to carbene and alkene or continue, via bond formation, to the product cyclopropane[9a] or (2) direct formation of the cyclopropane in a single step, entropy-controlled reaction, where $-\Delta S$ rises steadily while ΔH either rises insignificantly or falls as one proceeds along the reaction coordinate.[15]

Consider Scheme I, in which these mechanisms are depicted. In the "complex" mechanism, the extent of bond formation (i.e., one bond or two) and the nature of bond formation (i.e., biradical or polar) are not known. In the simplest description, considering only the product-forming step, the biradical intermediate should result in a moderately negative volume of activation, accompanied by little or no solvent effect. The dipolar intermediate should also afford a moderately negative volume of activation, but it should give rise to significant solvent effects.

At first glance, one imagines that the one-step pathway will lead to a large negative volume of activation with little solvent dependence. For example, one-step, nonpolar, two-bond-forming cycloadditions, such as the Diels–Alder reaction, are often characterized by volumes of activation on the order of ca. -40 cm^3/mol, whereas stepwise cycloadditions with rate-determining single-bond formation display volumes of activation about half as large.[1] However, pressure-dependence studies suggest that the transition state of the Diels–Alder reaction is "late" in terms of the positions of atomic nuclei, i.e., the volumes of activation and of reaction are similar.[1a] As a result, the Diels–Alder reaction may be quite irrelevant as a model for the carbene/alkene additions of Table I, since the temperature-dependence studies of the carbene reactions indicate that the product-forming cyclopropanation step has a significant negative activation entropy and low activation enthalpy, which are consistent with an early transition state.

In the case of the reversible formation of an intermediate carbene/alkene complex, the pressure dependence of the observed rate constant represents (Scheme I) a dependence both on the equilibrium constant (k_1/k_{-1}) for complex formation and on the rate constant for conversion of complex to product (k_2). The equilibrium constant for complex formation and the rate constant for cyclopropane formation are expected to increase with increasing pressure and therefore to possess associated negative volumes of activation. However, the rate constant for dissociation of the complex should also possess a large but unknown positive activation volume of special interest because of its potential similarity to the ubiquitous encounter complex invoked in all bimolecular reactions.

The pressure dependence of the rate constant for diffusion is known[16] for MCH, so that our data can be analyzed in terms of the reversibly formed complex mechanism by correction of the data for diffusion. In this way (see Table II for data) the dependence of k_{-1}/k_2 with pressure can be obtained.[17] The resulting analysis for TME as the alkene substrate yields $\Delta\Delta V^{\ddagger} = \Delta V_{k_{-1}}^{\ddagger} - \Delta V_{k_2}^{\ddagger}$. The values of $\Delta\Delta V^{\ddagger}$ (based on the assumption that $\Delta V_{k_2}^{\ddagger}$ corresponds to the activation volume for diffusion in MCH)[17c] obtained are 48, 39, and 36 cm^3/mol for PhCF, PhCCl, and PhCBr, respectively. Although numerous assumptions are required for the extraction of the activation volumes, if the analysis is valid, it would be the first time to our knowledge that information concerning the pressure effect on the dissociation of loosely bound complexes (in the limit, encounter complexes) has been obtained from kinetic analysis. In any case, the data appear to be consistent with the complex mechanism but do not require such an interpretation.

The absence of a significant solvent effect on the volume of activation for the addition of phenylchlorocarbene with tetramethylethylene (Table I) is evidence that the observed volumes represent the inherent volumes of activation ($\Delta V_{int}^{\ddagger}$). The observation also suggests that the zwitterionic pathway does not play an important role in the reaction mechanism, since an effect of solvent polarity would be expected in this case. If these assumptions are correct, the magnitudes of the observed volumes of activation are either those for a single-step reaction or for a preequilibrium with a biradical intermediate together with a bond-forming step.

Although the Diels–Alder reaction is conventionally viewed as possessing an early, "starting material-like" transition state, because of the low activation energies generally found for this family of reactions, pressure studies suggest that the transition state is late as far as the positioning of atomic nuclei are concerned, i.e., the volumes of activation and the volumes of reaction are similar. As a result, we cannot differentiate the reversible complex mechanism from the single-step mechanism if the latter is characterized by loose bond formation or an early transition state.

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(17) (a) For a similar analysis of a 1,3-dipolar cycloaddition reaction see: Yoshimura, Y.; Osugi, J.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 680. (b) These figures are calculated by a quadratic analysis. Plots of ln (k_{-1}/k_2) vs. pressure are almost linear and provide values of $\Delta\Delta V^{\ddagger}$ found to be 34, 34, and 30 cm^3/mol for PhCF, PhCCl, and PhCBr, respectively. (c) The activation volume for diffusion in MCH from the pressure dependence of the solvent viscosity was calculated to be +25 cm^3/mol.

The very low activation energies for the addition of carbenes to alkenes would seem to require an early transition state, but it is mute with respect to the degree of bonding. Clearly, a very early transition state might lead to relatively small activation volumes even if a two-bond-forming mechanism were involved.

Another aspect of our data which requires comment is the observation that for the faster reacting carbenes the plots of rate data vs. pressure are curved, whereas for the slower reacting carbenes the plots are linear in the pressure range investigated. We attribute at least part of the curvature for the more reactive carbenes to the influence of pressure on diffusion. The compression of MCH is such that over the pressure range 0.1 to 200 MPa, the rate of diffusion is expected to decrease by a factor of ca. 6. For the faster reacting carbenes this means that reactivity is becoming more and more controlled by diffusion as the pressure is increased. For the more slowly reacting carbenes the effect of pressure in this range does not introduce a significant contribution of diffusion-controlled quenching to the rate as a function of pressure. As further evidence for this conclusion, the slope of the rate constant/pressure curve for the reaction of phenylchlorocarbene with TME in acetonitrile is linear over the pressure range 0.1 to 203 MPa, whereas the analogous slope in MCH is sharply curved. The change to linearity is expected because the rate constant for diffusion, estimated from the viscosity in acetonitrile (1.9×10^{10} M^{-1} s^{-1} at 0.1 MPa), is larger than that in MCH (9.7×10^{9} M^{-1} s^{-1} at 0.1 MPa) and the pressure dependence of MCH on viscosity is larger than that of acetonitrile.[16] These observations suggest that the subtraction of the diffusion effects referred to above to obtain $\Delta\Delta V^{\ddagger}$ is valid. However, diffusion is probably not the only source of curvature in the plots of ln k_q vs. pressure; our upper limit for k_q for the reaction of PhCCl with TME is ca. 5×10^{8} M^{-1} s^{-1}.

Conclusions

The observed rate constants for the reactions of arylhalocarbenes with alkenes are accelerated by the application of moderate pressures. The magnitude of the activation volumes falls in the range -10 to -18 cm^3/mol for rate constants that vary from ca. 5×10^{8} to ca. 1×10^{6} M^{-1} s^{-1} and are not sensitive to solvent. These results appear to rule out a late, two-bond transition state and a bipolar single-bond transition state, but they are consistent with the reversible formation of a carbene-alkene complex or an early one- or two-bond transition state.

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Macrolide Formation by Free Radical Cyclization

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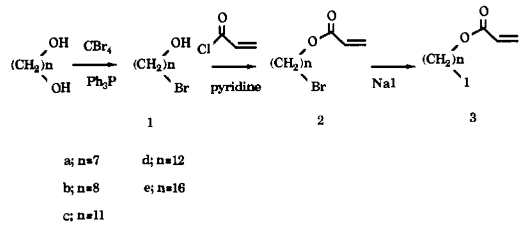
Abstract: A method for the synthesis of lactones with ring size greater than 11 members has been developed. The method involves intramolecular free radical addition to acrylate or fumarate esters. Thus, α,ω-halo alcohols are converted to the acrylate esters and the lactone is formed by treatment of the iodoalkyl acrylates with Bu_3SnH. Products formed are exclusively endocyclic. Yields of lactone are on the order of 55–88%, as analyzed by gas chromatography (45–78% isolated yields) for synthesis of rings greater than 15 members. Yields for 11–13 membered rings are lower and significantly more acrylic products are isolated for these systems. Cyclization to fumarate esters occurs in both the exo and endo mode, the endocyclic product being preferred by as much as 5/1 over the exocyclic compound. The ratio of endo/exo products is reduced to nearly 1/1 as the ring size is increased to 20. Rates of cyclization for the acrylate esters are on the order of 2×10^{4} s^{-1}.

Many natural products contain lactone substructures of 12 to 20 members, and these macrolides are of immense importance in the pharmaceutical industry.[1] Because of the importance of these compounds as antibiotics, an extensive effort has been made to develop methods for macrolide synthesis and highly successful approaches have been reported. Methods utilized from C—O, C=C, or C—C bonds in the crucial ring-making reactions with perhaps the most extensive literature involving formation of the lactone from acyclic ω-hydroxy acid derivatives.[2-4] More recent approaches utilize palladium coupling[5] or anionic cyclizations[6] to promote C-C bond formation.

Free radical methods are becoming increasingly important in organic synthesis, and successful methods for construction of 5- and 6-membered rings by radical cyclization are now an established part of the synthetic repertoire.[7,8] Thus, extensive investigations have focused on studies of the mechanism and synthetic applications of cyclopentane ring construction by radical intermediates. Intermolecular free radical addition reactions have also been studied extensively, and Giese's pioneering work has brought a new level of understanding to this field.[9,10] Steric and electronic effects dominate the mode of radical addition, and Giese's studies provide quantitative information about the nature of alkene substituents and how they influence radical additions to the double bond.

Scheme I



We reasoned that radical cyclization would be a potentially useful means of construction of large ring compounds. Our reasoning was based on the fact that $k_{\text{intramolecular}}/k_{\text{intermolecular}}$ values

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