Table IV. Pseudo-First-Order Rate Constants of $ZnCl_2$-Catalyzed Reactions of 1 with 2 in Dichloromethane (–70 °C) in the Presence of Different Donors[a]

donor	$k_{1\psi}$, s^{-1}	k_{rel}
diethyl ether	1.02×10^{-3}	1.00
ethyl acetate	2.99×10^{-4}	0.29
acetone	2.49×10^{-5}	0.024
tetrahydrofuran	1.17×10^{-6}	0.0011
tetrahydropyran[b]	4×10^{-6}–4×10^{-7}	$\sim 10^{-4}$
dimethyl sulfoxide	no reaction	
pyridine	no reaction	

[a] 7.34 mmol of $ZnCl_2$ (0.103 mol/L), 18.9 mmol of donor, 2.47 mmol of **1** and 25.0 mmol of **2**. [b] No first-order kinetics.

Other Donor Solvents. Some other $ZnCl_2$ donor complexes which are soluble in CH_2Cl_2 have been examined with respect to their catalytic activity. At a donor/$ZnCl_2$ ratio of 2.57, the ether complex exhibited the greatest relative catalytic activity (Table IV). The Me_2SO and pyridine complexes are so stable that no reaction was observed at –70 °C.

Conclusion. Addition of ether increases the solubility of $ZnCl_2$ in dichloromethane and thus enhances the catalytic activity of the Lewis acid. In systems with $[Et_2O]/[ZnCl_2] \approx 0.5$ the reactivity is 10^3–10^4 times higher than in ether free systems. Reactions, which take more than 6 weeks in $ZnCl_2$–CH_2Cl_2 systems, are complete within 1 h if 0.5 equiv of ether are added! More ether reduces the catalytic activity of $ZnCl_2$ because of complexation. The little sensitivity of the $ZnCl_2$–Et_2O system toward moisture facilitates its synthetic applications. Since a zeroth reaction order of $[ZnCl_2]$ is found at $[Et_2O]/[ZnCl_2] = 2.5$–4.0 over a wide range of concentrations, an increase of the $ZnCl_2$–Et_2O quantity is usually not helpful to accelerate a reaction.

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Registry No. 1, 2051-90-3; 2, 763-29-1; 3, 96761-10-3; $ZnCl_2$, 7646-85-7.

Notes

Concerning the Mechanism of Isomerization of *cis*-Azoalkanes

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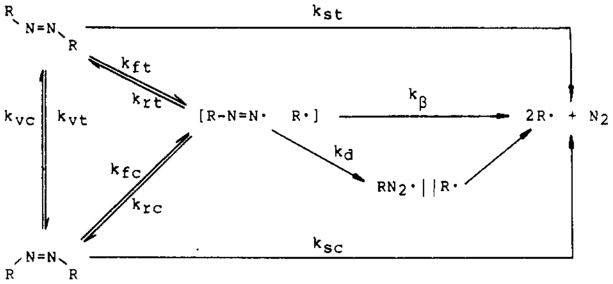
The mechanism of thermal decomposition of azoalkanes has been the subject of many investigations in recent years. Much of the discussion has focused on the unresolved question of whether a synchronous, two-bond cleavage process (k_s) or a two-step, one-bond cleavage process via short-lived diazenyl radicals ($k_f < k_\beta + k_d > k_r$) is operative (Scheme I).[2,3] Neuman and co-workers[4,5] have employed high pressure techniques to determine the volumes of activation for such processes and consider the latter to be a good mechanistic discriminator. They[4,5] found typical values of between +12 and +20 cm^3 mol^{-1} for a two-step radical formation mechanism, compared to values of between +2 and +5 cm^3 mol^{-1} for synchronous two-bond scission processes. Preliminary investigations in our laboratories[6] on the pressure dependence of the thermal deazatization reactions of a series of *trans*-azoalkanes resulted in volumes of activation which fitted well into the two categories mentioned above, viz., $C_6H_5N{=}NC(CN)_2CH_3$, $\Delta V^{\ddagger} = +11.9 \pm 0.8$; $C_6H_5C(CH_3)(C_2H_5)N{=}NC(CH_3)(C_2H_5)CH_3$, $\Delta V^{\ddagger} = +12.8 \pm 2.3$; $NCC(CH_3)(C_2H_5)N{=}NC(CH_3)(C_2H_5)CN$, $\Delta V^{\ddagger} = +2.9 \pm 0.5$ cm^3 mol^{-1}. Recently, the possible participation of *cis*-azoalkanes during the deazatization of *trans*-azoalkanes has been suggested.[7-10] Theoretical MNDO calculations[11] on the thermal decomposition of *cis*- and *trans*-azoethane and 1,1-diethyldiazene not only suggest that the step-wise mechanism is preferred to the synchronous two-bond cleavage process but also indicate that the cis transition state is common to both the cis and trans isomers, i.e., *trans*-azoethane first isomerizes and then looses N_2.

Scheme I



v - inversion
s - synchronous
d - diffusion
r - radical pair recombination
f - radical pair formation
c - cis
t - trans

Similarly the mechanism by which *cis*-azoalkanes isomerize thermally is a subject of great controversy.[12] Various

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[1] (a) University of Frankfurt. (b) University of Freiburg.

[2] For an excellent review, see: Engel, P. S. *Chem. Rev.* **1980**, *88*, 99.

[3] Engel, P. S.; Gerth, D. B. *J Am. Chem. Soc.* **1983**, *105*, 6849.

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[11] Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529. The authors postulate a hardly acceptable activation barrier of 10 kcal mol^{-1} for the recombination of the radical pair.

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experiments and theoretical arguments[7,11-14] have been presented in favor of inversion of one R group through a nitrogen atom (i.e., semilinearization) rather than the alternative rotation about the N=N bond. In addition, Neuman et al.[4] added a further dimension to this problem by claiming that both the thermal deazatization and isomerization reactions of *cis*-azo-1-adamantane and *cis*-azo-1-methylcyclopentane proceed via intermediate diazenyl radicals, i.e., a two-step process. They[4] based their claim on volume of activation data and drew the general conclusion that in systems where diazenyl radicals are formed from *cis*-azoalkanes, which live long enough to recombine, these serve as isomerization intermediates.

We question the suggestion that isomerization reactions of symmetrical *cis*-azoalkanes proceed via intermediate diazenyl radicals. It is in this context that the chemistry of *cis*-azonorbornane is of particular interest.[7] The cis isomer is converted quantitatively to the trans isomer on heating at 80 to 100 °C and no traces of radical side products are observed.[7,15] Therefore, the formation and recombination of a 1-norbornyl diazenyl-1-norbornyl radical pair[4] can safely be excluded as mechanism for this isomerization process.[16] This conclusion is supported by our unsuccessful attempts to detect radical intermediates by ESR spectroscopy, CIDNP and spin-trapping experiments, and the independence of the observed rate constant on the viscosity of the medium.[18,19] We have measured the pressure dependence of the cis to trans isomerization of azonorbornane, and the results are summarized in Table I. A plot of ln $k_{\rm obsd}$ vs. pressure is linear within the experimental error limits and the corresponding volume of activation is +6.1 ± 0.2 cm^3 mol^{-1} at 85.0 °C. We have also determined the apparent molar volumes of both species using an Anton Paar DMA 02 digital densimeter thermostated at 25.00 ± 0.002 °C. These are 188.0 ± 1.5 and 199.5 ± 1.5 cm^3 mol^{-1} for *cis*- and *trans*-azonobornane in heptane, respectively.[20] It follows that there is a significant increase in volume in going from the cis to the trans species and the magnitude of $\Delta V^{\ddagger}$ tentatively suggests that the transition state lies approximately halfway along the reaction coordinate. However, such a direct correlation is complicated by the large difference in temperature for the two sets of data, viz., 85 °C compared to 25 °C. Nevertheless, the trend in the volume data is of significant importance.

Table I. Values of $k_{\rm obsd}$ as a Function of Pressure for the Cis to Trans Isomerization of Azonorbornane[a]

pressure, bar	$10^4 k_{\rm obsd}$,[b] s^{-1}
50	1.74 ± 0.07 [c]
500	1.62 ± 0.07
100	1.43 ± 0.09
1500	1.31 ± 0.05
2000	1.17 ± 0.06

[a] Temperature = 85.0 °C, solvent = heptane + 1% DABCO, [azonorbornane] = 6.4 × 10^{-3} M. [b] Mean value of at least four kinetic runs performed in a Teflon holder within a high pressure cell. Samples were withdrawn with the aid of a sampling valve and analyzed spectrophotometrically at 424 nm. [c] In good agreement with kinetic data obtained under similar conditions at ambient pressure.[7]

The present results are in good agreement with the earlier suggested semilinearization mechanism[7] in terms of which the isomerization process is accompanied by a volume increase along the reaction coordinate. It is difficult at this stage to assign this volume increase to intrinsic changes only, and a solvent-dependence study of both $\Delta V^{\ddagger}$ and $\Delta \bar{V}$ is required to determine the solvational contribution. The results of the earlier performed solvent dependence study at ambient pressure[7] suggest rather small solvent effects, such that intrinsic volume changes may well be the prevailing contribution for the isomerization of *cis*-azonorbornane. In this respect it is important to note that Neuman et al.[4] reported the same volume of activation for the isomerization of *cis*-azo-1-adamantane in hexane and ethanol. On the other hand, solvational changes due to changes in the dipole moment of the molecule could for instance partly account for the slightly negative volumes of activation reported by Asano and co-workers[13,14] for a series of isomerization reactions, which were all suggested to proceed via an inversion mechanism. In a recent study these workers[21] reported large negative activation volumes for the isomerization of azobenzenes in polar solvents and explain these by the intervention of rotational isomerization.

It is, however, important to note that the volume of activation for the isomerization of *cis*-azonorbornane is very close to that found by Neuman and Binegar[4] for the isomerization of *cis*-azo-1-adamantane via the suggested radical pair mechanism. This would suggest that an inversion (semilinearization) mechanism could also be operative in the case of *cis*-azo-1-adamantane and that it is unnecessary to invoke a radical-pair mechanism on the basis of the volume of activation data.[4] This discrepancy is of fundamental importance and calls for a more detailed discussion.

Neuman et al.[4] base their conclusions on the fact that the volume of activation for cis to trans isomerization via a radical-pair mechanism, $\Delta V^{\ddagger}(k_{\rm i})$, is expected to be significantly smaller than the volume of activation for deazatization, $\Delta V^{\ddagger}(k_{\rm N_2})$, and should be comparable to $\Delta V^{\ddagger}(k_{\rm fc})$. However, we do not prefer to treat the pressure dependence data according to their[4] approach, since it involves the pressure dependence of the term

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(18) When the isomerization of *cis*-1-azonorbornane was conducted in mesitylene with or without added 9,10-dihydroanthracene at 110–130 °C, no norbornane product (detection limit 0.1%) was detectable by capillary gas chromatography. This is in agreement with reports in the literature.[12,15] When the isomerization was performed in the cavity of an ESR spectrometer in *tert*-butylbenzene between 364 K and 384 K, no signal was observed. In CIDNP experiments at 110 °C in pyridine-d_5, no enhanced absorption or emission signals were detected. In spin-trapping experiments with nitrosobenzene and *N*-*tert*-butyl phenyl nitrone between 330 K and 370 K, no signals which could be assigned to spin adducts of the 1-norbornyl radical were detected and no significant differences to the blank experiments were observed. The observed rate constant remained constant within the experimental error limits when the viscosity of the medium was increased approximately 5 times in going from heptane to hexadecane as solvent. The importance of cage effects can be demonstrated by such data in case diffusion (i.e., $k_{\rm d}$) plays a significant role.

(19) Kaiser, J.; Schmittel, M.; Limbach, H.-H.; Ruchardt, C., unpublished results.

(20) A range of concentrations (2 to 8 mM) was studied for each species and the apparent molar volumes were averaged since they showed no significant concentration dependence.

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$$\ln\left(1+\frac{k_{rc}}{k_{rt}}+\frac{k_{N_2}}{k_i}\right)$$

which they assumed to be small. Alternatively, it follows from the suggested mechanism[4] (included in Scheme I) that

$$k_{N_2}/k_i = (k_\beta + k_d)/k_{rt} \qquad (1)$$

and

$$\Delta V^{\ddagger}(k_{N_2}) - \Delta V^{\ddagger}(k_i) = \Delta V^{\ddagger}(k_\beta + k_d) - \Delta V^{\ddagger}(k_{rt}) \qquad (2)$$

The pressure dependencies of k_β, k_d, and k_{rt} will therefore determine the value of $\Delta V^{\ddagger}(k_{N_2}) - \Delta V^{\ddagger}(k_i)$ and the validity of the suggested mechanism. If $k_d \gg k_\beta$, then $\Delta V^{\ddagger}(k_\beta + k_d) \sim \Delta V^{\ddagger}(k_d)$ and could have a value as large as +18 cm^3 mol^{-1} for a solvent like hexane, since k_d is inversely proportional to the viscosity of the solvent.[4] On the other hand, if $k_\beta \gg k_d$ then $\Delta V^{\ddagger}(k_\beta + k_d) \sim \Delta V^{\ddagger}(k_\beta)$, and we expect this to be very close to $\Delta V^{\ddagger}(k_{fc})$ due to the similar nature of the reactions involved. A reasonable estimate for $\Delta V^{\ddagger}(k_{fc})$ is +5 cm^3 mol^{-1},[4] such that $\Delta V^{\ddagger}(k_\beta + k_d)$ could have a value between +5 and +18 cm^3 mol^{-1}.

The value of $\Delta V^{\ddagger}(k_{rt})$ strongly depends on the partial molar volumes of the cis and trans species, i.e., $\bar{V}_c$ and $\bar{V}_t$, respectively, as well as the location of the transition state for this process. Considering the mechanism in Scheme I, it follows that $\Delta\bar{V} = \bar{V}_t - \bar{V}_c = \Delta V^{\ddagger}(k_{fc}) - \Delta V^{\ddagger}(k_{ft}) = 0$[22] when $\bar{V}_t = \bar{V}_c$. Under such conditions $\Delta V^{\ddagger}(k_{rt})$ must be close to zero. Alternatively, $\Delta V^{\ddagger}(k_{rt}) \sim -\Delta V^{\ddagger}(k_{fc}) = -5$ cm^3 mol^{-1} when both processes (denoted by k_{rt} and k_{fc}) have late (product-like) transition states. However, in this study we clearly indicated that $\bar{V}_t$ and $\bar{V}_c$ are not necessarily equal and $\Delta\bar{V}$ could have a value between 10 and 12 cm^3 mol^{-1}. This brings about that $\Delta V^{\ddagger}(k_{rt})$ could have values between zero and +7 cm^3 mol^{-1} under the limiting conditions outlined above. It follows that $\Delta V^{\ddagger}(k_{rt})$ can vary between −5 and +7 cm^3 mol^{-1} depending on the nature of the transition state and the partial molar volumes of the reactant/product species.

Substitution of these limiting values for $\Delta V^{\ddagger}(k_\beta + k_d)$ and $\Delta V^{\ddagger}(k_{rt})$ in eq 2, indicates that $\Delta V^{\ddagger}(k_{N_2}) - \Delta V^{\ddagger}(k_i)$ can have values between zero and +23 cm^3 mol^{-1} for the suggested radical-pair mechanism. The experimental difference[4] of +12 cm^3 mol^{-1} is therefore no proof for the suggested radical-pair mechanism. On the other hand, we cannot rule out this mechanism on the basis of volume of activation data alone. Our present investigation clearly demonstrated that a very similar $\Delta V^{\ddagger}(k_i)$ value can be obtained for systems where radical-pair formation can be ruled out. It follows, as mentioned before, that it is unnecessary to invoke a radical-pair mechanism to account for the volume of activation data reportd before[4] and that a semilinearization mechanism can describe the process equally well. Furthermore, the observed volume of activation for the isomerization of *cis*-azonorbornane is in good agreement with the observed overall volume change, which encourages us to extent our arguments to the systems studied by Neuman et al.[4]

A recent paper[3] reported that only a very small fraction of adamantyldiazenyl radicals recombine at the primary end of the dimethylallyl radical. In the diazenylalkyl mechanism obtained for azoadamantane,[4] the observed 57% N_2 yield requires that 43% of the adamantyldiazenyladamantyl radical pairs recombine to give *trans*-azoadamantane. This large difference between the adamantyl and dimethylallyl systems favors the more likely explanation that isomerization proceeds overwhelmingly by inversion while loss of nitrogen goes via diazenyl radicals.[23]

We do not consider the investigated system to be atypical. The fact that the isomerization of azonorbornane occurs at a significantly higher temperature than the other studied systems[4] does not necessarily suggest a change in mechanism. The high reaction temperature results from the low heat of isomerization for this compound, viz., 17.1 compared to 28.4 and 28.2 kcal mol^{-1} for *cis*-1-azoadamantane and *cis*-1-azobicyclo[2.2.2]octane, respectively.[24] Furthermore, it is known from the literature that the relative rates of radical formation decrease in the order 1-adamantyl > 1-bicyclo[2.2.2]octyl > 1-norbornyl.[25]

It follows from this study that $\Delta V^{\ddagger}$ measurements alone cannot unequivocally pinpoint a mechanism in these systems. Combining such data with partial molar volume data for reactant and product species enables volume equation calculations and the construction of reaction volume profiles which assist the mechanistic assignment. The latter techniques have been applied with significant success in the elucidation of inorganic reaction mechanisms in recent years.[26]

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Registry No. *cis*-Azodi-1-norbornane, 59388-64-6.

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(22) In this treatment it is assumed that the partial molar volume of the radical pair is close to that of the common transition state for both processes.

(23) We are grateful to Prof. P. S. Engel for calling our attention to this fact.

(24) The isomerization enthalpies were calculated by using the MM1 force field method as extended to azo compounds by Crans and Snyder (*Chem. Ber.* 1980, *113*, 1201). Preliminary experimental results in our laboratories support these data.

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Deformation Density and Dissociation Energy of Strained C–C Bonds

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In a covalent bond the shared density binds the nuclei. Thus, the amount of deformation density determines, in some way, the bond strength. Bader et al.[1] have shown that there is a direct relationship between chemical bond strength (dissociation energy) and the magnitude of electrostatic field due to charge redistribution. They have shown that in diatomic homonuclear molecules the plot of the overlap and atomic contributions multiplied by $(1/R_e^2)$ vs. the dissociation energy is described by a linear relationship.

In the deformation density calculated by using IMO (iterative maximum overlap) hybrid functions, the pre-

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