Pressure Effects in Solvolysis and Solvolytic Fragmentation. A Correlation of Activation Volume with Concertedness[1]

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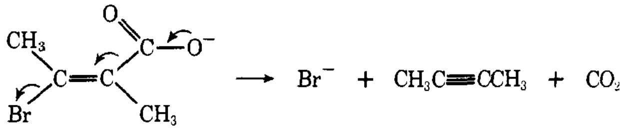
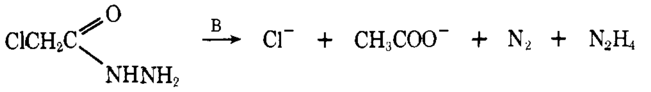
Abstract: The activation volume has been measured for the solvolysis of several γ-amino alcohol derivatives and their carbon analogues. After small corrections are applied for differences in reaction temperature and leaving group, the average value for the simple solvolysis reactions (SN1, E1, F1) in 80% aqueous alcohol at 40.0° is -21.5 ± 1.8 cm^3/mol, in excellent agreement with earlier results. In one of the γ-chloroamines (*trans*-**15**), the rate and products suggest that the effect of the nitrogen atom is purely inductive, and in this case $\Delta V_0^\ddagger$ is within the range of that of the solvolyses. In all other instances there is nitrogen assistance of one sort or another (N-4 participation, E_i elimination, F_c fragmentation); in all these cases $\Delta V_0^\ddagger$ is less negative by 5–10 cm^3/mol. In the concerted fragmentations, $\Delta V_0^\ddagger = -13.3 \pm 2.0$ cm^3/mol. Concurrent solvolysis and concerted fragmentation lead to intermediate values of $\Delta V^\ddagger$. The uses and limitations of the activation volume as a general criterion for concertedness are discussed.

The concertedness of multiple bonding changes continues to be a matter of great interest to organic chemists.[3] Since bond making and bond breaking are processes that are clearly reflected in the volume, and since the effect of pressure on rate constants allows one to calculate the so-called activation volume,[4] a number of chemists have sought to gauge concertedness in their reactions by means of the effect of pressure on the rates. The first attempt at such a correlation was made by Walling and Peisach:[5] their results for the Diels–Alder reaction led to polemics,[6] which left the issue in doubt until Grieger and Eckert[7] showed convincingly that the volume decrease in the transition state is close to that for the overall reaction: that fact alone strongly suggests that the reaction is a concerted one. In recent years a number of additional reports of the pressure effect in Diels–Alder reactions have appeared, and without exception these papers have described large pressure induced accelerations of the rates and improvements of the yields.[8]

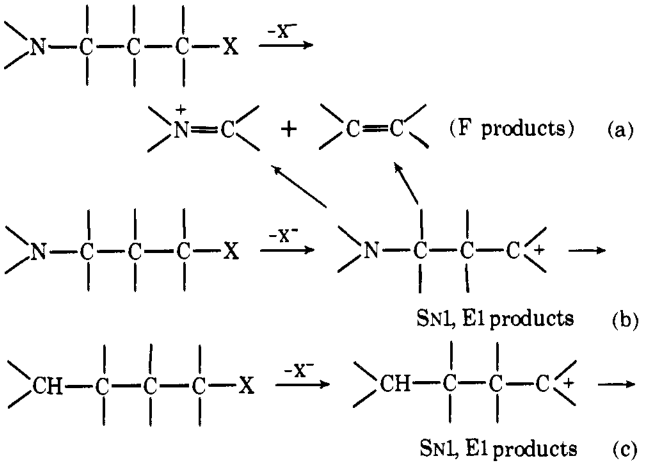
In view of the importance of the problem, our own approach has been to test the relation of concertedness and $\Delta V_0^\ddagger$ by means of reactions in which there is no doubt about the nature of the reaction. The first study[9] was that of the decarboxylation of β-bromoangelate to give bromide, carbon dioxide, and 2-butyne, a reaction several orders of magnitude faster than that of the Z isomer, β-bromotiglate; $\Delta V_0^\ddagger$ for the reaction was found to be +18 cm^3/mol, approximately double that of simple decarboxylations.[10] It may be noted in passing that, in this example, $\Delta V_0^\ddagger$ differs in sign from that of the Diels–Alder reaction, since simultaneous bond cleavages rather than bond formations are involved. In a second instance, the base-induced reaction of chloroacetyl hydrazide was studied; this reaction gives hydrazine, nitrogen, and chloride and acetate ions. The nature of products strongly suggested this reaction to be a concerted fragmentation;[11] however, $\Delta V_0^\ddagger$ was found to be -5 cm^3/mol, and subsequently a conventional study showed that it is a fragmentation only in a formal (product) sense, reaching the product stage by a highly circuitous route.[12]





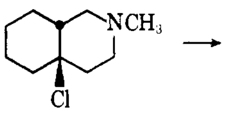
$$\mathrm{ClCH_2C}\genfrac{}{}{0pt}{}{\diagup O}{\diagdown NHNH_2} \xrightarrow{B} \mathrm{Cl^-} + \mathrm{CH_3COO^-} + \mathrm{N_2} + \mathrm{N_2H_4}$$

The present study concerns yet another heterolytic fragmentation reaction,[13] namely the solvolytic decomposition of γ-amino alcohol derivatives. This reaction can take place by a concerted mechanism (a) and by a two-step process (b), i.e., via a γ-amino carbonium ion:[14]

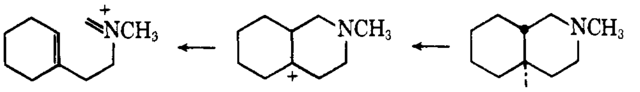


The principal evidence for the concerted nature of most of these reactions is the fact that, in spite of the inductive effect of the nitrogen atom, they are as much as 10^4 times faster than the solvolyses of the corresponding homomorphs (reaction c). Since the nitrogen atom is rigidly held in a position remote from the site of ionization in our examples, direct participation by the nitrogen lone pair cannot be the reason for the acceleration. The rate of the two-step process b, however, is invariably lower than that of the homomorph. This is due to the inductive effect of the nitrogen atom which hinders the formation of the γ-amino carbonium ion.

In the case of diastereoisomeric γ-chloroamines, such as *cis*- and *trans*-10-chloro-*N*-methyldecahydroisoquinoline (**15**) the driving force for concerted fragmentation, i.e., the frangomeric effect,[14] can be derived from a comparison of the individual rate constants.[15] Whereas *cis*-**15** fragments quantitatively by the concerted mechanism a, the *trans* isomer, for stereoelectronic reasons, reacts by way of the carbonium ion **17**, and elimination products are formed beside the fragmentation product **16** (50%).



cis-**15**



16 **17** *trans*-**15**

The rate-controlling step in all three reactions (a, b, and c) produces a pair of ionic charges, and hence $\Delta V_0^\ddagger$ is expected to be negative in sign in spite of the breaking bonds; the electrostriction accompanying the formation and solvation of ionic charges in condensed phases is well known to be large and to outweigh the positive contribution of bond cleavage to $\Delta V_0^\ddagger$ by a wide margin.[16] Thus, it may be expected that $\Delta V_0^\ddagger$ will be negative in both the concerted and stepwise fragmentations a and b and in the simple solvolysis c, but less so in the concerted fragmentation a.

Besides the convincing nature of the evidence for concertedness in solvolytic fragmentation, this reaction offered another major advantage from our point of view. It is well known that it is difficult to make precise measurements of $\Delta V_0^\ddagger$ in reactions that are strongly affected by pressure;[17] in fact, the polemics mentioned above were probably based on faulty results caused by this difficulty. The solvolytic reaction can readily be followed by means of conductance measurements. This technique for measuring rate constants is not only more precise than most others, but it can be used continuously while the solution is under pressure.

This advantage is tempered somewhat by the necessity of using the Guggenheim procedure,[18] and hence of making conductance measurements over a period of many half-lives. In view of the wide range of rates characterizing the series of substrates of interest to us, it furthermore proved necessary to compare pressure effects on reactions over the rather wide temperature range of 60° and with substrates differing in leaving group. Fortunately, these two variables have been encountered in several other studies,[16a] and a correction can be made for them. So far as temperature induced changes in $\Delta V_0^\ddagger$ are concerned, an experimental value of 0.08 cm^3/(mol °C) was found (see below). The literature reveals that these changes are dependent on the type of reaction; however, if we limit ourselves to reactions that generate ions in water or aqueous organic media, an average temperature coefficient of 0.07 ± 0.03 cm^3/(mol °C) is obtained for ten cases,[19] in agreement with our own measurement. Concerning the difference in $\Delta V_0^\ddagger$ between reactions in water or aqueous organic media which differ only in whether chloride or bromide ion is produced, the recent data of Swaddle[20] suggest a value of 1.2 cm^3/mol; this value is in good agreement with the average (1.3 ± 0.7) calculated on the basis of the difference in electrostriction volume between these two ions.[20d] Both the raw data and the standardized activation volumes are recorded below, so that revisions can readily be made should later insights suggest them.

Experimental Section

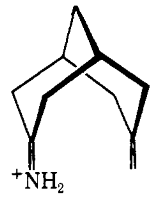
The apparatus[21] and the application of the conductance technique under pressure have been described. The syntheses and rate constants for the compounds used in this study (**1** to *cis*-**15**) are reported elsewhere. References to these reports are included in the text below; a review summarizing most of these results has appeared.[14]

Results and Discussion

The results are reported in Table I, which shows the number and structure of each substrate, the mechanistic type, the temperature, the observed activation volume, and $\Delta V_0^\ddagger$; the latter values are obtained from the preceding ones by means of the corrections described above.

As a check on our procedures, we began by measuring the solvolysis rate of *tert*-butyl chloride in 80% aqueous alcohol at 30.00°. In this reaction, Hyne et al.[23] have reported $k_1 = (1.90 \pm 0.03) \times 10^{-5}$ s^{-1}; our own value is $(1.896 \pm 0.003) \times 10^{-5}$ s^{-1}.

We start by comparing compounds **1** and **2**.[24] In 80% aqueous alcohol, amine **2** solvolyzes more rapidly than **1** by a factor of 30 in spite of the inductive power of the amino group and in spite of the fact that the nitrogen lone pair cannot participate directly, i.e., through space. Also, while **1** is simply converted into the alcohol and ethyl ether, **2** gives exclusively the ring-opened product **18**. These facts are hard to reconcile with anything save a concerted fragmentation of **2**. The activation volumes of these two bromides are −20.3 and −16.1 cm^3/mol, respectively. Thus, the extra (positive) volume requirement of the additional breaking bond is clearly reflected in $\Delta V_0^\ddagger$ (as noted by a referee, loosening of a hydrogen bond at N would also have this effect). Similarly, **3** and **4** react solvolytically with a rate ratio of about 1:500[24] and that of **5** and **6** is about 1000.[25] Compounds **4** and **6** clearly fragment by the concerted mechanism. For both pairs, $\Delta\Delta V_0^\ddagger$ is about 7-10 cm^3/mol. Compounds **7**[26] and **8**[27] also react much faster than their homomorphs by factors of 5×10^4 and 1.3×10^4, respectively; $\Delta V_0^\ddagger$ for these reactions is −13.6 and −15.4 cm^3/mol. The enormous rate ratios made it impossible to measure the activation volumes for the corresponding carbon compounds.

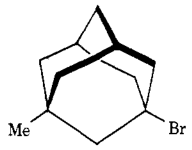
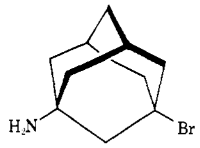
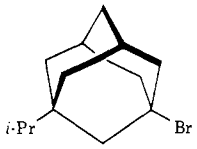
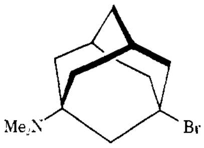
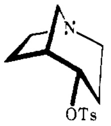
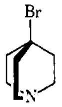
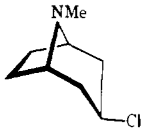
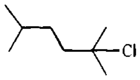
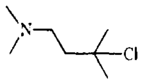
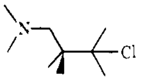
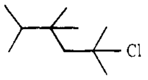
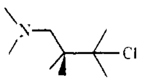
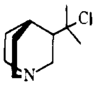
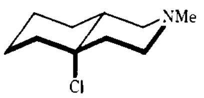


18

The five limiting solvolyses (SN1-E1) in Table I have an average standard activation volume of −21.5 ± 1.8 cm^3/mol. This compares very well with some of our earlier results; thus, Shurpik[22] found −20.7 ± 0.4 cm^3/mol for the solvolysis of five sample benzenesulfonates in aqueous acetone at 25°C (hence, −21.9 cm^3/mol at 40.0°). *tert*-Butyl chloride at 30.0° in 80% aqueous alcohol has a value[23] of −22.2 cm^3/mol, hence −21.8 cm^3/mol if referred to present conditions. With a solvolysis rate constant nearly five times *smaller* than that of its homomorph and a $\Delta V_0^\ddagger$ of −23.8 cm^3/mol, *trans*-**15** also belongs in this category. These results once again underscore the remarkable uniformity of activation volumes within a given reaction type. The five concerted fragmentations of **2**, **4**, **6**, **7**, and **8** lead to an average value of −13.3 ± 2.0 cm^3/mol, and hence we conclude that the extra breaking bond makes a contribution of $\Delta V_0^\ddagger$ of about +8 cm^3/mol.

We may now consider the question of whether the data reveal any further detail. The earlier survey[14] had shown that the rate ratio for the γ-haloamine and its homomorph may vary from 0.12 to 50 000. In the former extreme, the amine (e.g., *trans*-**15**) reacts by the two-step mechanism b and gives solvolysis beside fragmentation products. In several other instances where solvolysis accompanies fragmentation, the rate ratio is less than 1 but larger than 0.5. Entries **10**[28] and **14**[29] are of this type, with rate ratios of

Table I. Activation Volumes for the Solvolytic Reactions of Several Substrates in 80% Aqueous Ethanol[a]

No.	Compound	Mechanistic type	Temp. °C	$\Delta V_0{}^{\ddagger}{}_{\mathrm{obsd}}$, cm³/mol[b]	$\Delta V_0{}^{\ddagger}$, cm³/mol[c]
1		SN1	50.0	−21.11	−20.3
2		F_c[d]	49.6	−16.84	−16.1
3		SN1	50.0	−20.32	−19.5
4		F_c	21.3	−10.45	−11.9
5		SN1, E1	60.0	−21.83	−20.2
6		F_c	12.4	−7.43	−9.6
7		F_c	49.6	−14.39	−13.6
8		F_c	49.6	−17.36	−15.4
9		SN1, E1	39.3	−23.77	−22.6
10		F_c, F1,[e] SN1, E1	39.3	−18.19	−17.1
11		F_c, N-4	49.6	−18.02	−16.1
12		SN1, E1	10.0	−23.63	−24.8
13		F_c, E_i[f]	2.2	−8.05	−9.9
14		F_c, F1, SN1, E1	15.0 25.0 35.0	−16.34 −17.11 −17.92	−15.4
15		F1, E1	65.5	−27.10	−23.8

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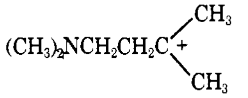
[a] Each reaction was measured at eight pressures between 0 and 1 kbar. [b] $\Delta V_0{}^{\ddagger}{}_{\mathrm{obsd}}$ was determined by fitting $\ln k_p/k_0$ to $a + bp + cp^2$ and by the use of $\Delta V_0{}^{\ddagger}{}_{\mathrm{obsd}} = -bRT$. The correlation coefficients were in all cases 0.9970 or better (0.9991 on the average for all the reactions shown here); it is estimated that $\Delta V_0{}^{\ddagger}{}_{\mathrm{obsd}}$ is accurate to ±0.3 cm³/mol. [c] All values in the preceding column referred to a standard leaving group (bromide) and temperature (40°); see text. [d] Concerted fragmentation. [e] Two-step fragmentation. [f] Anchimerically assisted elimination.

0.52 and 0.65, respectively; the activation volumes are −17.1 and −15.4 cm^3/mol, respectively. These data suggest that in **10** and **14** the concerted process a and the two-step process b are occurring simultaneously.

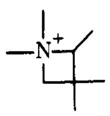
This has recently been shown for **10**.[30] Thus, in 40% ethanol at 25°, this compound undergoes 32.5% fragmentation besides 41% substitution (SN1), 25% elimination (E1), and 1.5% cyclization. In the presence of more than 2.0 M potassium azide, the yield of fragmentation products (isobutene, dimethylamine, and formaldehyde) drops to 24%, due to the trapping of the γ-aminocarbonium ion **19** by azide ion. Therefore, at least 8%, and probably more, fragments by the two-step mechanism b, i.e., via the cation **19**. It should, in principle, be possible to measure $\Delta V_0^\ddagger$ for both simultaneous reactions by an appraisal of the pressure effect on the product distribution; however, this has not been done.



$(CH_3)_2NCH_2CH_2\overset{CH_3}{\underset{CH_3}{C^+}}$

19

Compound **11** produces chloride ion some 4000 times faster than its homomorph, but in this case the azetidinium salt **20** is obtained as the main product (80%) beside 20% of fragmentation products. This result was explained on the basis of concurrent N-4 assisted cyclization and concerted fragmentation.[31] This is supported by the activation volume, which is −16.1 cm^3/mol in this case; lowering of $\Delta V_0^\ddagger$ values due to participation and charge dispersal in the transition state has been described before.[20e]



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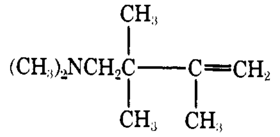
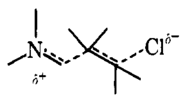
Finally, **13** is an intriguing example. It solvolyzes 125 times faster than the homomorph, yielding 70% of fragmentation products and 30% of the aminoolefin **21**.[32] The relative rate and the product composition reveal that both reactions are accelerated by the nitrogen atom. It was therefore concluded that in this case concerted fragmentation is accompanied by anchimerically assisted elimination.[32] The transition states for these reactions, **22** and **23**, respectively, show similar charge dispersal. It is therefore not surprising that the activation volume, namely −9.9 cm^3/mol, is similar to the average value for concerted fragmentation.



$(CH_3)_2NCH_2\overset{CH_3}{\underset{CH_3}{C}}\text{—}\underset{CH_3}{C}{=}CH_2$

21



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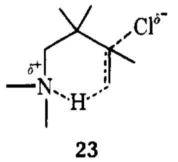

23

The overall trend in the data is that any sort of nitrogen assistance, however modest in its rate enhancement, has a large and unmistakable effect on $\Delta V_0^\ddagger$. It might at first sight appear odd that this effect on the activation volume does not keep pace with the effect on the rate ratio once this assistance is becoming substantial. In order to understand why the relation between $\Delta\Delta V_0^\ddagger$ and $\Delta\Delta G^\ddagger$ ($RT \ln k/k_h$) need not simply be linear, one should realize that $\Delta V_0^\ddagger$ is a function of both the degree of bond cleavage and of charge delocalization. The contribution of bond cleavage to $\Delta V_0^\ddagger$, as noted above, is uniformly positive; i.e., the further it proceeds, the larger the positive contribution to the activation volume—up to perhaps +10 cm^3/mol. The second factor, that of charge delocalization, also makes a positive contribution to $\Delta V_0^\ddagger$, but this contribution reaches a maximum at a delocalization of 50% (perhaps +5 cm^3/mol) and goes back to zero in those instances in which the charge is completely relocalized to the nitrogen atom (and hence no longer dispersed).[33] Since it is not known exactly how the bond lengthening and the delocalization are matched, it cannot be predicted with any certainty how these two factors will add up over a range of substrates; the difference in activation volume with that of the SN1 reactions would be expected to become pronounced as the rate ratio begins to be significantly larger than one, but it should level off or even reach a maximum before extreme rate accelerations are observed—as the data tend to show.

While the data concerning the Diels-Alder and fragmentation reactions do, indeed, seem promising, there are some pitfalls in this connection that have not been pointed out in the literature, and hence we conclude this paper on a cautionary note. It is convenient to do so in terms of the cycloadditions; the subsequent discussion assumes that the volume is a reasonable measure of the reaction coordinate.[34] The simple discussions of activation volumes in one-step vs. two-step reactions generally make three assumptions that are not specifically mentioned. The first of these is that, given a stepwise reaction, the transition state preceding the intermediate is higher in energy than the one following, and hence that *its* formation is rate controlling; second, that the one-step transition state will be more product-like than the first transition state in the two-step reaction; third, that solvent effects may be neglected. If any one of these assumptions fails, there is no basis for relating the mechanisms to $\Delta\Delta V_0^\ddagger$. Thus, if the second transition state has an energy comparable to or even higher than that of the first, then if anything the criterion should be reversed, with the stepwise reaction having a more product-like activated complex. A situation of this sort involves the reversible formation of the intermediate ("return"), and, in fact, a complication of this sort has been shown to be present[35] in some [2 + 2] cycloadditions though not in all of them.[36] Return has also complicated the study of concertedness in perester decompositions.[37] The second assumption is the really vital part of the criterion; however, there is no law of nature forbidding reactant-like activated complexes in concerted reactions, or product-like first transition states in stepwise reactions. In other words, the criterion is based on intuition rather than on axiomatic necessity. Finally, if the intermediate and the transition states leading to it have zwitterionic rather than diradical character, electrostriction may well cause reversal of the criterion. Examples have been discovered, for example, by Mukhtar,[38] who found pressure to favor a [2 + 2] cycloaddition over the competing homo-Diels-Alder reaction; by Neuman,[39] who found concerted perester decomposition to be retarded abnormally little by pressure in those cases where the radicals seemed likely to have polar character; and by Kelm, who found an exceedingly large negative activation volume in the cyclobutane formation from TCNE and enol ethers.[35b] Fortunately, solvent effects may in such cases reveal the zwitterionic character.

In conclusion, we note here that concertedness in the solvolytic fragmentation reaction can be demonstrated by means of high-pressure kinetics as it can in the Diels-Alder reaction; however, the applicability of this criterion depends on several assumptions which should always be considered explicitly.

Acknowledgment. The work described here was generously supported by the National Science Foundation.

References and Notes

(1) Paper XXXVII in the series "Kinetics of Reactions in Solutions Under Pressure". Presented in part at the 4th International High Pressure Conference in Kyoto, Japan, Nov 1974.
(2) (a) At Stony Brook; (b) at Basel.
(3) For recent discussion, see (a) J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972); (b) F. G. Bordwell, *ibid.*, **3**, 281 (1970).
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Multiple Fluorescences. II. A New Scheme for 4-(*N*,*N*-Dimethylamino)benzonitrile Including Proton Transfer[1a]

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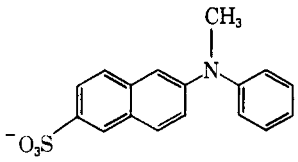
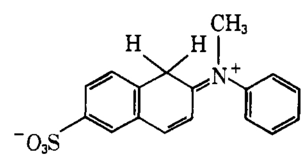
Abstract: Long-wavelength emission from 4-(*N*,*N*-dimethylamino)benzonitrile is assigned to a protonated molecule (deuterium isotope effect). Utilizing solvent polarity parameters, three other emissions are identified: planar monomer, perpendicular monomer, and dimer. The protonated emitting species occurs only in proton-donor solvents; the ratio of monomer protonated molecule emissions is viscosity and wavelength dependent.

The "abnormal" emission from *N*-methyl-2-(*N*-phenylamino)-6-naphthalenesulfonate in glycerol has been identified as that of a protonated molecule.[1a] The expected emission appeared only if the photochemical conversion to **2** were avoided, consistent with protonation occurring in the S^*_0 state, and vibrational relaxation in a high-viscosity solvent being sufficiently slow to encounter competition from a proton-transfer process, that converting structure **1** into structure **2**.



1



2

The two emissions from excited 4-(*N*,*N*-dimethylamino)benzonitrile [1-cyano-4-(*N*,*N*-dimethylamino)benzene,