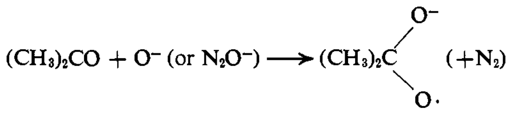
solute effect different from that observed in the γ-ray reaction. Electron transfer from I to acetone leads only to a change of identity and would therefore not be expected to be a chain-terminating process. No decreases in yields were in fact observed in the presence of a large excess of acetone in the present work. The inhibition observed in the γ-ray reaction is not readily explicable in terms of the proposed chain mechanism, but a possible rationalization of this anomalous behavior is given elsewhere.[3]

Complete inhibition of the γ-ray reaction brought about by nitrobenzene and benzophenone was accompanied by the formation of a previously unobserved product, carbon monoxide.[3] No carbon monoxide was detectable in the DTBP-photoinitiated reaction in the presence of these solutes. A possible explanation is that the concentration required to inhibit completely the formation of nitrogen and methane would result in essentially all the light being absorbed by these solutes and none getting through to DTBP. However, it is interesting to note that in the case of complete inhibition by carbon tetrachloride, a significant yield of carbon monoxide was observed. A mechanism for the formation of carbon monoxide is not readily formulated.

The constancy of the ratio of the yields of nitrogen to methane is consistent with these two products resulting from a common precursor, the formation of methane constituting a side reaction of the main chain. The oxygen radical anion (formed *via* reactions 1 and 2) is initially in close proximity to an acetone molecule since N_2O^- is short-lived.[15] Reactions such as 12–14 may therefore be probable and would also account for the observed formation of potassium acetate.



$$(CH_3)_2CO + O^- \text{ (or } N_2O^-\text{)} \longrightarrow (CH_3)_2C(O^-)(O\cdot) \quad (+N_2) \qquad (12)$$

III

$$\text{III} \longrightarrow CH_3\cdot + CH_3CO_2^- \qquad (13)$$

$$CH_3\cdot + (CH_3)_2CHOH \longrightarrow CH_4 + \text{II} \qquad (14)$$

The formation of nitrogen in the photolysis of alkaline solutions containing benzophenone and nitrous oxide is consistent with radical anion I, an intermediate in the photoreduction of benzophenone in alkaline 2-propanol,[6,7] bringing about the decomposition of nitrous oxide (reaction 1). The parallel dependence of the nitrogen yields on the concentrations of nitrous oxide and potassium hydroxide in the benzophenone- and DTBP-initiated reactions supports the conclusion that essentially the same chain reaction is involved in both systems. The fact that the kinetic chain length for a given initiator concentration is smaller in the benzophenone reaction than in the DTBP reaction would appear to indicate that benzophenone also acts as a chain terminator, its efficiency being greater than that of DTBP. The observation that benzophenone is more effective than DTBP in retarding the γ-ray reaction[13] supports this suggestion, as does the result (Table III) that a small concentration of benzophenone will retard the DTBP-photoinitiated chain.

Acknowledgments. The experimental work was carried out during the tenure of an Israel Atomic Energy Commission Fellowship. The author wishes to thank Dr. Arie Rajbenbach for many helpful discussions.

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(14) The facility with which nitroaromatics and diaryl ketones undergo electron-transfer reactions with organic anions has been documented by G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(15) F. S. Dainton, *Radiation Res., Suppl.*, **4**, 71 (1964).

The Initial-State Contribution to the Activation Volume for Benzyl Chloride Solvolysis

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Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada. *Received October 19, 1966*

Abstract: The first-order rate constants for the solvolysis of benzyl chloride in aqueous methyl, isopropyl, and *t*-butyl alcohols are reported at 50.25° and various pressures up to 4000 atm. The activation volume is calculated from these data and is seen to exhibit extremum behavior with solvent composition in each of the systems studied. The partial molal volume of the initial-state substrate, benzyl chloride, in each of the solvents and in the aqueous ethyl alcohol solvents of ref 1 is measured and shown to account for the major part of the extremum behavior. The solvent dependence of the partial molal volume of the transition state is shown to be remarkably similar to that of various inorganic salts in the same solvents.

In a previous publication[1] we reported a study of the effect of pressure on the solvolysis of benzyl chloride in aqueous ethyl alcohol. It was found that, as the alcoholic content of the solvent increases, the activation volume at atmospheric pressure, $\Delta V_0^{\ddagger}$, exhibits extremum behavior similar to that previously reported for the activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$.[2] At that time no data were available to indicate whether variations in the volume of the initial or the transition state, or both, are responsible for the extremum behavior.

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(1) J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Am. Chem. Soc.*, **88**, 2104 (1966).

(2) J. B. Hyne, R. Wills, and R. E. Wonkka, *ibid.*, **84**, 2914 (1962).

The activation enthalpy behavior as a function of solvent composition for the solvolyses of *t*-butyl chloride, *t*-butyldimethylsulfonium iodide, and methyl benzenesulfonate in aqueous ethyl alcohol has been partially dissected into initial and transition state contributions by Arnett, *et al.*[3–5] In the case of *t*-butyl chloride it was found that the greater part of the extremum behavior in $\Delta H^{\pm}$ as a function of solvent composition is due to variation of the solvation enthalpy of the initial state for *t*-butyl chloride.[4] The residual variation due to the transition state was found to be relatively minor and somewhat complex.[4]

A similar dissection of the activation volume into the initial- and transition-state contributions depends upon the ability to measure the partial molal volume of the initial state in the solvolytic medium (eq 1). Knowing the partial molal volume of the initial state, $\bar{V}_g$,

$$\Delta V_0^{\pm} = \bar{V}_t - \bar{V}_g \tag{1}$$

and the activation volume, $\Delta V_0^{\pm}$, the partial molal volume of the transition state, $\bar{V}_t$, can be determined.

In this paper we report the rate data for benzyl chloride solvolysis in a series of alcohol–water mixtures, other than the ethyl alcohol system previously studied,[1] as a function of both pressure and solvent composition. A method for determining the partial molal volume of the initial state "instantaneously" is described and checked against the data of Mitchell and Wynne-Jones[6] for the partial molal volume of water in aqueous ethyl alcohol. It is found that the $\Delta V_0^{\pm}$ extremum behavior observed in each solvent system is largely the result of extremum behavior in the partial molal volume of the initial state, $\bar{V}_g$.

Experimental Section

Kinetics. The high-pressure apparatus and techniques for determining rates as a function of pressure were described previously.[1]

Partial Molal Volumes. The technique used here is essentially the dilatometric method of Shinoda and Hildebrand.[7] The main modification in the present study was the use of a syringe to inject the solute into the dilatometer rather than the sealed capillary employed by the original authors.

Apparatus. The dilatometers consisted of 100-ml bulbs containing a magnetic stirring bar and fitted with a 6-in. length of 0.7-mm i.d. precision bore capillary. These were calibrated by weighing the amount of mercury they held and by measuring the molal volume of water in water by the method described below. A standard 25-μl syringe, fitted with a Chaney adapter and a 6-in., 27-gauge needle, was used for injecting the solute. The stop was set at 5 μl, and the exact volume delivered was determined by weighing the amount of water delivered on a microbalance.

A thermostat of similar design to those employed for the kinetic runs[1] was used. However, the main nichrome heater was omitted as it was found to be unnecessary for the small thermostat (about 3-gal capacity); the front wall consisted of a sheet of plate glass to facilitate reading of the meniscus in the dilatometer. It was found that two propellor-type stirrers, at different levels in the oil, were necessary in order to prevent fluctuation of the dilatometer meniscus due to temperature gradients. It is to be noted that a polyethylene shield around the thermostat reduced the effect of air drafts and was helpful in minimizing fluctuation of the meniscus due to ambient temperature changes.

A magnetic stirrer was modified by removing the controls to a point some distance down the power cord, and the stirrer itself was enclosed in a lead-weighted Perspex box which was lowered into the thermostat.

Method. The calibrated dilatometer was filled with the appropriate solvent mixture and allowed to attain thermal equilibrium in the thermostat. The capillary meniscus reading served as a sensitive guide to this condition. Necessary adjustments in the position of the meniscus were made by adding or removing solvent with a 6 in., 27-gauge needle syringe. The benzyl chloride solute was loaded into the microsyringe to the 5-μl position of the Chaney adapter. The syringe needle was then inserted into the dilatometer capillary in such a manner as to ensure delivery into the body of the bulb of the dilatometer. Alignment of the microsyringe and capillary was maintained by a special clamp holder. Reequilibration of temperature was obtained in several minutes as indicated by the constancy of the meniscus reading. It should be noted that the presence of the syringe needle within the dilatometer capillary acts as a very significant amplifier for the sensitivity of the dilatometer. The volume of the capillary is markedly reduced, and only the annular space between the needle and the inner walls of the capillary need be filled by the expanding liquid.

The observed volume change on injecting the solute is equal to the change in height of the meniscus, *h*, multiplied by the cross-sectional area of the annular space between the capillary wall and the hypodermic needle. Having calibrated the capillary, as described above, its radius, r_c, is known, and the radius of the needle, r_n, was measured with a micrometer. The observed volume change is therefore given by

$$\Delta V_{\text{obsd}} = \pi h(r_c^2 - r_n^2) \tag{2}$$

Injection of the known amount of solute and dissolution in the solvent, aided by the use of the magnetic stirrer, was normally very rapid; from the known rates of solvolysis of the solute in the various solvents, it can be shown that the amount of solvolysis taking place between injection and final meniscus reading is negligible. The partial molal volume can be evaluated from the known amount of solute injected and the meniscus readings before and after injection.

Results

Rates. The conductance data were analyzed by the method of Guggenheim[8] using a least-squares calculation.[1] The observed first-order rate constants are presented in Table I.

Activation Volumes. The volumes of activation were calculated by fitting the experimental rate–pressure data to eq 3 using the method of least squares.[1] It has been

$$\ln k = A + Bp + Cp^2 \tag{3}$$

shown previously[9] that eq 3 generally describes rate–pressure data better than any of the other available empirical functions. The standard deviation shown in Table II illustrates the relative reliability of the four analytical methods discussed in ref 9 when applied to the reaction of present interest in the four solvent systems studied in this paper and in the previous publication.[1] The standard deviation is defined as

$$\text{std dev} = \sqrt{\frac{\Sigma(\ln k_{\text{obsd}} - \ln k_{\text{calcd}})^2}{n-1}} \tag{4}$$

for the linear,[9] quadratic,[9] and Benson–Berson analyses,[10] and as

$$\text{std dev} = \sqrt{\frac{\Sigma\,[\ln (k_{n+1}/k_n)_{\text{obsd}} - \ln (k_{n+1}/k_n)_{\text{calcd}}]^2}{n-1}} \tag{5}$$

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[3] E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Am. Chem. Soc.*, **85**, 1350 (1963).

[4] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

[5] E. M. Arnett, W. G. Bentrude, and P. M. Duggleby, *ibid.*, **87**, 2048 (1965).

[6] A. G. Mitchell and W. F. K. Wynne-Jones, *Discussions Faraday Soc.*, **15**, 161 (1953).

[7] K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **62**, 295 (1958).

[8] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[9] H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne, *Can. J. Chem.*, **44**, 2193 (1966).

[10] S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962).

Table I. Rate Constants for the Solvolysis of Benzyl Chloride at 50.25° in Aqueous Alcohol at Various Pressures

Mole fraction of alcohol	Pressure, atm				
	1	681	1362	2723	4084
	$10^5 \times k$, sec^{-1} [a]				
			Methyl Alcohol		
0.100	12.47 ± 0.04	17.49 ± 0.04	23.1 ± 0.4	44.0 ± 1	
0.200	7.045 ± 0.005	10.7 ± 0.4	13.92 ± 0.01	23.09 ± 0.06	
0.300	3.731 ± 0.008	5.9 ± 0.1	8.124 ± 0.009	14.01 ± 0.02	
0.400	2.035 ± 0.005	3.31 ± 0.02	4.826 ± 0.003	8.773 ± 0.007	11.7 ± 0.4
0.500	1.246 ± 0.002	2.00 ± 0.03	3.01 ± 0.01	5.40 ± 0.01	8.37 ± 0.04
			Isopropyl Alcohol		
0.100	2.094 ± 0.005	3.71 ± 0.03	5.74 ± 0.03	10.96 ± 0.01	14.7 ± 0.1
0.200	0.462 ± 0.001	0.77 ± 0.02	1.24 ± 0.01	2.20 ± 0.03	4.20 ± 0.01
0.300	0.2174 ± 0.0004	0.387 ± 0.008	0.58 ± 0.01	0.91 ± 0.04	1.71 ± 0.05
0.400	0.1288 ± 0.0001	0.187 ± 0.003	0.270 ± 0.009	0.46 ± 0.01	0.88 ± 0.06
			t-Butyl Alcohol		
0.100	0.679 ± 0.006	1.33 ± 0.06	2.35 ± 0.04	4.45 ± 0.02	7.79 ± 0.03
0.200	0.1868 ± 0.0002	0.33 ± 0.01	0.50 ± 0.04	0.950 ± 0.003	1.252 ± 0.004
0.300	0.0910 ± 0.0005	0.149 ± 0.003	0.17 ± 0.05	0.459 ± 0.002	0.692 ± 0.008

[a] Values in pure water and in various ethyl alcohol–water mixtures can be found in ref 1.

Table II. Standard Deviations for Benzyl Chloride Solvolysis at 50.25° in Aqueous Methyl, Ethyl, Isopropyl, and *t*-Butyl Alcohols

Method	Std dev
Linear	0.1110
Quadratic	0.0403
Benson–Berson	0.0515
Incremental	0.0783

for the incremental slope analysis.[9] Again, in the present instance, the quadratic analysis is seen to produce the best results.

The activation volume, defined as[11]

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial p}\right)_{\mathrm{T}} \tag{6}$$

is, at atmospheric pressure, given by (see eq 3)

$$\Delta V_0^{\ddagger} = -RTB \tag{7}$$

The values of this parameter for each solvent composition studied are presented in Table III along with the uncertainties as calculated by the method described previously.[1,9]

Table III. Activation Volume for the Solvolysis of Benzyl Chloride at 50.25°[a]

Mole fraction of alcohol	$\Delta V_0^{\ddagger}$, ml/mole		
	Methyl alcohol	Isopropyl alcohol	*t*-Butyl alcohol
0.100	−12.13 ± 0.06	−23.1 ± 0.2	−25.5 ± 0.1
0.200	−15.6 ± 0.2	−19.0 ± 0.1	−22.7 ± 0.8
0.300	−17.9 ± 0.1	−18.1 ± 0.5	−17 ± 3
0.400	−19.8 ± 0.5	−13.62 ± 0.04	
0.500	−18.8 ± 0.2		

[a] The values for pure water and aqueous ethyl alcohol mixtures are in ref 1.

Partial Molal Volumes. Since the solutions used in this study were very dilute (about 5×10^{-4} *m*), it was assumed that they could be treated as being infinitely dilute so that the apparent molal volume could be taken as the partial molal volume of the solute.

From the known volume delivered by the syringe, and from the known density of the solute (benzyl chloride[12] and water[13]) at *room* temperature, the weight, and therefore the number of moles, *n*, of the solute delivered to the solution can be calculated. The partial molal volume of the solute is then given by[7]

$$\bar{V} = \Delta V_{\mathrm{obsd}}/n \tag{8}$$

The data of Table IV show that the assumption of infinite dilution is a reasonable one. Seven successive injections of the solute in the same solvent sample gave similar results, within experimental error, and no trend is apparent which would be indicative of solute–solute interactions.

Table IV. Partial Molal Volume of Benzyl Chloride in 0.4 Mole Fraction of Ethyl Alcohol at 50.25°

Trial	$\bar{V}_{\mathrm{PhCH_2Cl}}$, ml/mole
1	117.81
2	117.00
3	116.59
4	117.00
5	117.97
6	117.08
7	117.32
Average	117.25 ± 0.38[a]

[a] The average deviation from the mean.

In order to test the accuracy of this method, the partial molal volume of water was measured in the various aqueous ethyl alcohol solvents used in our study.[1] Satisfactory agreement between our results and those of Mitchell and Wynne-Jones[6] is shown in Figure 1.

The partial molal volume of benzyl chloride in the various solvents pertinent to this study is given in Table V. Since the insolubility of benzyl chloride in

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(11) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(12) A. I. Vogel, *J. Chem. Soc.*, 644 (1948).

(13) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1933, p 25.

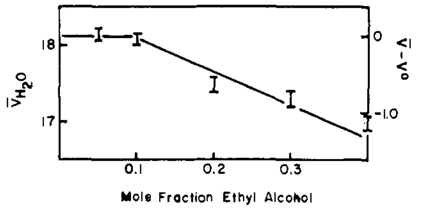

Figure 1. Partial molal volume of water in aqueous ethyl alcohol. Points are present data; line is from ref 6.

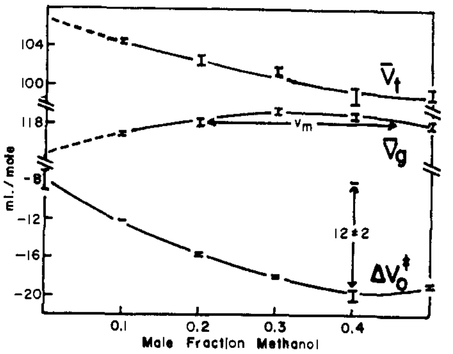

Figure 2. Volume parameters for benzyl chloride solvolysis in aqueous methyl alcohol.

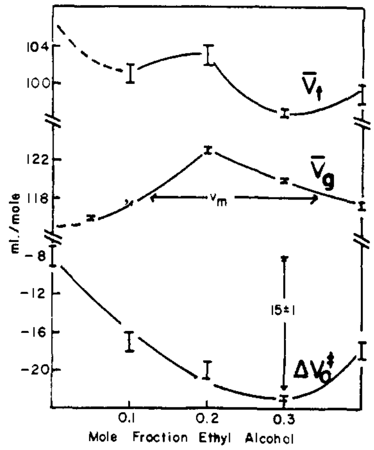

Figure 3. Volume parameters for benzyl chloride solvolysis in aqueous ethyl alcohol.

water prevented the determination of $\bar{V}_g$ in this solvent, the value was determined by extrapolation of the four $\bar{V}_{PhCH_2Cl}$ *vs.* mole fraction alcohol curves and was found to be 115 ml/mole.

Discussion

Activation Volumes. The dependence of $\Delta V_0^{\ddagger}$ on solvent composition is shown in Figures 2–5 for each of the solvent systems reported here and for the previously reported ethyl alcohol system.[1] In each instance minimum values are observed, and the extremum size and position are dependent upon the nature of the organic solvent component. This same behavior has been observed previously for the activation enthalpy of *p*-methylbenzyl chloride solvolysis in various aqueous–organic solvent systems,[14] the depth of the minimum generally increasing as its position approaches pure water.

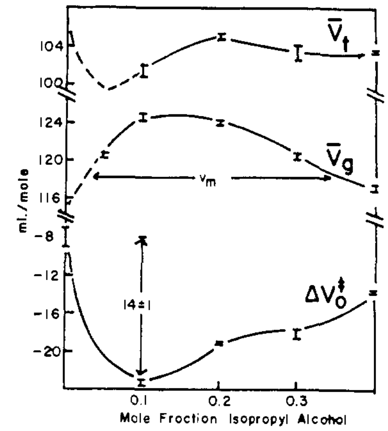

Figure 4. Volume parameters for benzyl chloride solvolysis in aqueous isopropyl alcohol.

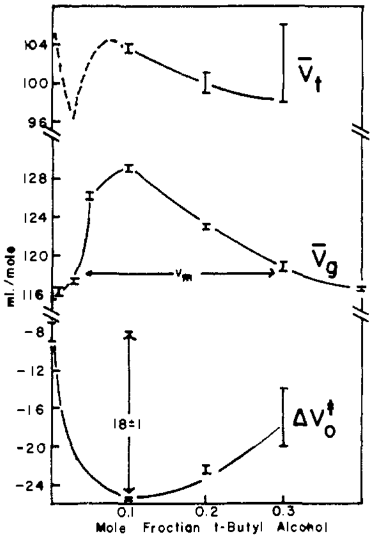

Figure 5. Volume parameters for benzyl chloride solvolysis in aqueous *t*-butyl alcohol.

Tommila, *et al.*,[15–17] did not observe activation enthalpy minima in aqueous methyl alcohol and concluded that the organic solvent component had to

Table V. Partial Molal Volume of Benzyl Chloride in Aqueous Alcohol Mixtures at 50.25°[a]

Mole fraction of alcohol	$\bar{V}_{PhCH_2Cl}$, ml/mole Methyl alcohol	 Ethyl alcohol	 Isopropyl alcohol	 *t*-Butyl alcohol
0.010				115.2 ± 0.4
0.030				117.2 ± 0.3
0.050		116.0 ± 0.1	120.5 ± 0.3	126.2 ± 0.3
0.100	116.9 ± 0.2	117.5 ± 0.1	124.5 ± 0.4	129.1 ± 0.4
0.200	118.2 ± 0.3	123.1 ± 0.3	124.0 ± 0.3	123.0 ± 0.3
0.300	119.3 ± 0.3	119.9 ± 0.1	121.4 ± 0.3	118.8 ± 0.5
0.400	118.8 ± 0.3	117.3 ± 0.4	117.1 ± 0.2	116.5 ± 0.2
0.500	117.9 ± 0.4			

[a] Value in pure water as extrapolated from data in this table is 115 ml/mole.

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(14) J. B. Hyne and R. Wills, unpublished results.

(15) E. Tommila, A. Koivisto, J. P. Lyyra, L. Antell, and S. Heimo, *Ann. Acad. Sci. Fennicae, Ser. A II*, 47 (1952).

(16) L. Pekkarinen and E. Tommila, *Acta Chem. Scand.*, **13**, 1019 (1955).

(17) E. Tommila and S. Maltamo, *Suomen Kemistilehti*, **B28**, 118 (1955).

possess large hydrophobic groups in order that minima be observed.[18] We have found that a minimum does exist in the activation enthalpy for benzyl chloride solvolysis in aqueous methanol.[19] The fact that a minimum occurs in $\Delta V_0^{\ddagger}$ in aqueous methyl alcohol (Figure 2) further suggests that Tommila's conclusion is erroneous, and it would appear that the minima in the two activation parameters are due to similar factors.

Partial Molal Volumes. Initial State. As stated earlier, an understanding of the $\Delta V_0^{\ddagger}$ minima depends upon knowledge of the partial molal volume behavior of the two states involved in the activation process. The solvent dependence of the initial-state partial molal volumes, $\bar{V}_g$, is illustrated in Figures 2–5. It can be seen that maxima occur in this physical property at much the same positions as the minima in $\Delta V_0^{\ddagger}$. It is interesting to note that this volume maximum behavior parallels that for the heat of solution of various nonelectrolytes.[4] Such a parallelism supports both the reality of these maxima and the suggestion that they are mutually dependent upon the same physical phenomenon.

By definition, the partial molal volume of the solute is the change in volume of the *solvent* on addition of 1 mole of the solute to make an infinitely dilute solution. It is therefore apparent that the only physical significance to the value of $\bar{V}$ is the formation of holes, of sufficient size and shape to accept the solute molecules, and reorientation of the solvent molecules so as to obtain that configuration most favorable for interaction with the solute. This process of "hole making" and reorientation of the solvent molecules around the dissolved solute must be dependent on the degree of structure existing in the solvent medium prior to the dissolution process. Evidence has been cited recently,[20,21] demonstrating that the first additions of an organic cosolvent to water leads not to a reduction of inherent water structure, as might be expected intuitively, but rather to an *increase* in structuredness of the binary solvent system as a whole. Accordingly the dissolution process of benzyl chloride in pure water will be one of placing a solute molecule in a less structured medium compared with that of dissolving benzyl chloride in say a 0.1-mole fraction of alcohol in water solvent. Dissolution in the more structured medium might reasonably be expected to bring about a greater change in volume of the solvent since the hole-making process and solvent orientation will involve greater expansion of the structure. By this line of reasoning we can rationalize the observed *increase* in the partial molal volume, $\bar{V}_g$, as the organic content of the aqueous binary increases. Clearly, however, the added cosolvent cannot induce greater structure in the binary solvent medium indefinitely; there will therefore be a maximum structuredness attained, beyond which normal bulk effect disruption of structure will predominate. Beyond this point dissolution of the substrate benzyl chloride will be accompanied by a smaller change in volume of the solvent, and hence the maximum behavior of $\bar{V}_g$ as a function of solvent composition is observed.

Using the density of benzyl chloride at 50.25°[12] an estimate of the molal volume of the pure substrate may be made, $v_m = 118.1$ ml/mole. This value is indicated in Figures 2–5 on the $\bar{V}_g$ curves. It is seen that in each case the value of $\bar{V}_g$ near the maximum is greater than v_m, suggesting that, near the maximum, solvent structure disruption is somewhat greater than simply that required to accommodate the solute in a hole of minimal dimensions. This is compatible with the idea that at the maximum the solvent is highly structured and reorientation of the solvent environment around the hole may be quite specific and not such as to lead to minimal expansion required to accommodate the substrate. The apparent smaller value of $\bar{V}_g$ compared with v_m in pure water on either side of the maximum may be a manifestation of the "collapse" of the less structured solvent environment around the substrate in these cases. It must be pointed out, however, that the v_m value as obtained is the partial molal volume of benzyl chloride in pure benzyl chloride and may not be strictly applicable to benzyl chloride in solution; such factors as free volume contribution to v_m have been neglected and, consequently, v_m as used may be too large.

Transition State. By adding $\bar{V}_g$ to $\Delta V_0^{\ddagger}$, $\bar{V}_t$ is obtained (eq 1). The results of this addition can be seen in Figures 2–5. The broken-line sections of the curves are derived from interpolated values of $\Delta V_0^{\ddagger}$ and the experimental values of $\bar{V}_g$, the pure-water point being obtained in the reverse manner. It is apparent that only the methyl alcohol–water system gives a simple dependence of $\bar{V}_t$ on solvent composition. The other three curves are somewhat complex—even to the point of exhibiting relatively large minima for which the depth and position is a function of the size of the alcohol molecule. It can be concluded that the large maximum found in the $\bar{V}_g$ dependence on solvent composition accounts for most of the extremum in $\Delta V_0^{\ddagger}$ (100% in aqueous methyl alcohol, 70% in aqueous ethyl alcohol, and 50% in aqueous isopropyl and *t*-butyl alcohols). This is similar to the enthalpy behavior found in aqueous ethyl alcohol. Arnett, *et al.*,[3,4] found the $\Delta H^{\ddagger}$ minimum for *t*-butyl chloride solvolysis in aqueous ethyl alcohol to be largely due to the initial state. We have also observed that the transition state enthalpy for benzyl chloride solvolysis in aqueous ethyl alcohol shows no reflection of the minimum in $\Delta H^{\ddagger}$.[19]

It is interesting to compare the behavior of $\bar{V}_t$ with that of the partial molal volumes of various ionic species in the same solvent mixtures. Bateman's densities for barium chloride solutions in aqueous ethyl alcohol[22] permit the calculation of $\bar{V}_{\mathrm{BaCl_2}}$, and Padova[23] has measured the partial molal volumes of various metallic acetates in aqueous ethyl alcohol. The solvent dependence of the partial molal volumes of these salts and that of the benzyl chloride solvolytic transition state is shown in Figure 6 for aqueous ethyl alcohol.

All five of the curves in Figure 6 display very complex behavior which could well be described as a "roller-

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[18] E. Tommila and S. Maltamo, *Suomen Kemistilehti*, **B28**, 73 (1955).

[19] H. S. Golinkin, Ph.D. Thesis, The University of Calgary, 1966.

[20] F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966).

[21] E. M. Arnett, Symposium on Physico-Chemical Processes in Mixed Aqueous Solvents, Bradford, England, May 1966, to be published.

[22] R. L. Bateman, *J. Am. Chem. Soc.*, **74**, 5516 (1952).

[23] J. Padova, *J. Chem. Phys.*, **39**, 2599 (1963).

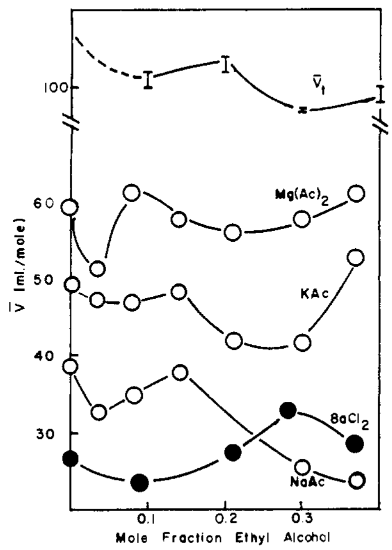

Figure 6. Comparison of the solvent dependence of the partial molal volume of the benzyl chloride solvolytic transition state with various salts in aqueous ethyl alcohol. The acetates are from ref 21 and barium chloride is from ref 20.

coaster" type. The fact that the benzyl chloride transition-state behavior is not unlike that of the electrolytes suggests that it is a pseudo-ionic entity. However, caution must be used in such a comparison. Association of the ions of the salts in the more alcoholic solvents may be great enough to persist to infinite dilution. The partial molal volumes of the salts would therefore be averaged values for the separated ions, undissociated salts, and, in the cases of magnesium acetate and barium chloride, partially ionized species. In pure water, on the other hand, each of the salts undoubtedly exists as dissociated ions. Obviously, the benzyl chloride transition state cannot be described as dissociated ions but may resemble some form of ion pair or highly developed dipole. Therefore, comparison of the transition state with the salts in the highly aqueous solvents must be fortuitous. Nevertheless, the similarity between the partial molal volume behavior of the benzyl chloride solvolytic transition state and each of the salts does suggest that the former is a highly polar species.

In summary, we have found that a minimum in $\Delta V_0^{\pm}$ as a function of solvent composition occurs in each of the aqueous alcohol systems studied and is mainly due to the behavior of the partial molal volume of the initial state. The partial molal volume of the transition state shows smaller, but more complex, dependence upon solvent composition than either $\bar{V}_g$ or $\Delta V_0^{\pm}$. The behavior of $\bar{V}_t$ for benzyl chloride solvolysis in aqueous ethyl alcohol parallels that of electrolytes, suggesting that the transition state is a highly polar species.

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The Microwave Spectrum and Dipole Moment of Pyrazole

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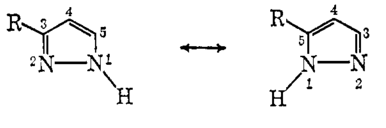
Abstract: The microwave spectrum of pyrazole in the region 8000 to 35,000 Mc/sec has been assigned. The rotational constants are $A = 9618.92 \pm 0.14$, $B = 9412.59 \pm 0.13$, and $C = 4755.88 \pm 0.11$ Mc/sec. The dipole moment, $\mu = 2.214 \pm 0.015$ D., was calculated from the Stark effect of the $0_{0,0} \rightarrow 1_{0,1}$ and $0_{0,0} \rightarrow 1_{1,1}$ transitions but only after the perturbation treatment had been extended to fourth order. The indicated uncertainties are three times the standard errors obtained from the least-squares fit. The interpretation of the data shows that in the gas phase pyrazole is a planar molecule with no in-plane symmetry axis.

Although pyrazole is a compound of great chemical interest and has been well studied, very little is known about the physical properties of pyrazole as an isolated molecule. Much of the interest has been concerned with the tautomerism of the pyrazoles substituted in the 3 and 5 positions. These structures are



found to be chemically indistinguishable[1] and, in nuclear magnetic resonance experiments, magnetically equivalent.[2,3] The indistinguishability of the 3- and 5-substituted pyrazoles was first explained by Knorr in 1894, who suggested that the proton was not bonded to just one of the nitrogen atoms but rather oscillated rapidly back and forth between both atoms and, if the temperature could be lowered sufficiently, the oscillation would stop and the two tautomers would become separable isomers.[4] This hypothesis was in fact reasonably close to the currently accepted description

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[1] J. D. Loudon, "Chemistry of Carbon Compounds," Vol. 4, Part A, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1957, p 249.

[2] I. L. Finar and E. F. Mooney, *Spectrochim. Acta*, **20**, 1269 (1964).

[3] N. C. Hung, Ph.D. Thesis, University of Rochester, Rochester, N. Y., 1962; University Microfilms Inc., Ann Arbor, Mich., Order No. 63-5978, pp 64–107.

[4] L. Knorr, *Ann. Chem.*, **279**, 188 (1894).