

Solvent Cage Effect in the Photolysis of Azomethane in Aqueous Alcohols and Other Media: A Semiempirical Correlation with Macroscopic Solvent Parameters¹

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Abstract: Photolyses of azomethane in aqueous *tert*-butyl alcohol media show a maximum yield of cage products in the range of solvent compositions near 0.9 mol fraction of water ($X_{\text{H}_2\text{O}}$ 0.9). In the range of 0.9 to 0.6 $X_{\text{H}_2\text{O}}$ the fraction of cage recombination of methyl radicals from the photolyses of azomethane decreases with increasing macroscopic viscosity. A semiempirical equation developed to treat these data is successful in relating the observed amount of cage product ethane to macroscopic solvent parameters other than viscosity (principally to solvent internal pressure and cohesive energy density). The correlation equation, derived using a phenomenological model, is successful in describing the cage effect in a wide range of solvent types for photolyses of azomethane carried out in this work and the decompositions of other radical initiators for which data are available in the literature. A new synthetic method, starting with the alkylation of diethyl sulfonyldicarbamate, is described which is suitable for the preparation of symmetrical or unsymmetrical azoalkanes.

In the years since Frank and Rabinowitch³ first advanced the idea of the solvent cage effect in radical-radical reactions much work has been directed toward studies of the relationships between the magnitude of this effect and the initiator structure, mode of initiator homolysis, temperature, pressure, and macroscopic solvent parameters such as viscosity and internal pressure.⁴ The efficiency of free-radical production (F) in the decomposition of an initiator has often been discussed⁵⁻⁹ in terms of an effective rate constant (k_d), which approximately describes the diffusional separation of caged radical pairs to give free radicals, a process competing with radical-radical reactions within the solvent cage.¹⁰⁻¹³ The prediction of solvent effects on k_d , as reflected in F , has been approached by considering the correlation between F and macroscopic solvent parameters such as solvent viscosity.⁵⁻⁹ An inverse dependence of k_d upon some power of solvent viscosity (η) (a dependence on $1/\eta^a$, where $0.5 < a < 1.0$) has been found in many studies.⁵

This appealingly simple approach has enjoyed remarkable success (both qualitative and quantitative) in correlating results of studies of the cage effect in nonassociated solvents or solvent mixtures showing small deviations from ideality, most commonly saturated hydrocarbon solvents of varying viscosity.

To develop a more general semiempirical relationship between cage effect and macroscopic solvent parameters we have chosen to carry out studies of the cage effect in the photolyses of azomethane in aqueous *tert*-butyl alcohol and aqueous methanol mixed solvents. The complex variation of solvent structure with solvent composition in these mixed solvents has been well documented.¹⁴⁻¹⁶ Our choice of these media for study was predicated on the notion that these should provide the most severe test of any semiempirical correlation, such as we were seeking, and provide the impetus for the development of a more general form of the correlation. Azomethane was chosen as the radical initiator for study since (a) it is very soluble in aqueous media, though uncharged, (b) it gives simple products, methane (from free radicals) and ethane (from caged radicals), whose relative abundance reflects the importance of the cage effect,^{17,18} and (c) the nonpolar methyl radical is not expected to be subject to strong specific interactions with solvent.

Many physical properties of highly aqueous binary solutions pass through extrema in the region above 0.80 mol fraction

water and these have been related to effects of solvent structuredness.¹⁴⁻¹⁶ To date highly aqueous *tert*-butyl alcohol solutions have given the most pronounced extrema of this kind,¹⁴⁻¹⁶ making this system very desirable for our study. The methanol-water system was also chosen for study since methanol is thought to dissolve into the water structure substitutionally in contrast to an interstitial dissolution in the case of *tert*-butyl alcohol.¹⁴ In the *tert*-butyl alcohol-water system, the macroscopic viscosity used in the usual formal treatment of the cage effect does not reflect the large changes in solvent structure seen in the highly aqueous region of this system. The present study of azomethane decomposition in these extremely nonideal systems shows that there are indeed serious difficulties in correlating initiator efficiency with bulk viscosities.

An understanding of the solvent cage effect in highly aqueous media is especially desirable in view of the accumulating body of evidence that free-radical reactions are important agencies for damage to living cells.^{19a} Evidence from NMR spectroscopy^{19b} that the degree of water structure in some malignant tumor cells is markedly different from that in normal cells adds significance to a study of the relationship between solvent structure in aqueous media and the cage effect. Radical-destroying cage reactions provide a route for the harmless removal of radical initiators without the generation of the free radicals which can damage living cells.

Experimental Section

General. *tert*-Butyl alcohol was boiled with sodium and distilled before purification by fractional freezing. Hydrocarbon solvents were purified by washing with H_2SO_4 and water, then drying and distilling. All other solvents were either spectroscopically pure or purified by distillation. All mass spectra were obtained from a Varian-Atlas CH-5 mass spectrometer.

Azomethane. Azomethane was synthesized by HgO oxidation of *sym*-dimethylhydrazine according to the method of Renaud and Leitch.²⁰ The azomethane was collected in a -78°C trap and stored in the dark.

Preparation and Photolysis of Azomethane Solutions. Solutions of 0.05 M azomethane in various organic solvents and aqueous *tert*-butyl alcohol and aqueous methanol were made by transferring the azomethane with a syringe into a weighed quantity of solvent in a -20°C cold room. Samples of between 20 and 30 μl of the solution were transferred to melting-point capillary tubes in which they were degassed and sealed under vacuum. About 50 of these capillaries were

suspended in a temperature-controlled ($\pm 0.1^\circ$) water bath and irradiated with a G. E. Sunlamp. The upper parts of the capillary tubes were blackened to minimize gas-phase decomposition of azomethane. The aqueous solutions were photolyzed over a period of 2–3 weeks, the organic solutions over a period of 1–2 days. Analyses of the contents of the capillary tubes with varying sizes of blackened gas-phase regions showed no variations in product ratios.

Gas Chromatographic Analysis. The relative amounts of methane and ethane produced from photolyses of the azomethane solutions were determined by flame ionization gas chromatography. A $\frac{1}{8}$ in. \times 9 ft Porapak Q column was used with a helium gas flow rate of 25 ml/min. Although a good separation of methane and ethane may be obtained at room temperature, the column was cooled with dry ice to lengthen the retention time of methane in order to obtain a more accurate integration of a broader peak. After the appearance of the methane peak (retention time, 3 min) the dry ice was removed and the column was allowed to warm to room temperature. Ethane appeared with a retention time of roughly 12 min. The capillary tubes containing the photolyzed solutions were broken inside the injector with a capillary tube crusher.

A standard gas sample containing equimolar amounts of ethane and methane and one containing equimolar amounts of ethane and methyl chloride were prepared by vacuum-line techniques and injected with a gas-tight syringe to calibrate the gas chromatographic analytical method.

Deuterium Labeling Experiments. A 4-ml portion of 0.99 or 0.90 mol fraction water-*tert*-butyl alcohol solution of an equimolar mixture of azomethane and azomethane- d_6 (0.05 M) was degassed and sealed in a 5-ml cylindrical Pyrex cell and irradiated at 6 $^\circ\text{C}$ using a G. E. Sunlamp. To prevent the gas-phase decomposition of azomethane, the upper region of the cell was blackened. After photolysis the cell was attached to the vacuum line and two traps cooled to -130°C were used to condense everything except ethane, methane, and nitrogen. The ethane was then condensed in a collection vessel cooled to -196°C and opened to the vacuum for short periods of time to remove methane and nitrogen. The sample was analyzed for C_2H_6 , C_2D_6 , and CH_3CD_3 by mass spectrometry at low ionizing voltages.

An equimolar mixture of azomethane and azomethane- d_6 (0.05 M) in 500 ml of CCl_4 was similarly photolyzed at 0 $^\circ\text{C}$ in an ice bath. Methane and nitrogen were collected as described above and analyzed for the isotopic distribution of methane by mass spectrometry. After collection of the methane-nitrogen mixture the traps were warmed from -196 to -78°C allowing collection of the ethane and methyl chloride, which were also analyzed by mass spectrometry.

Sulfamide. Sulfuryl chloride and ammonia were condensed according to the method of Degering and Gross²¹ to give sulfamide. Ethyl acetate was found to be superior to acetone in the extraction of product sulfamide from the ammonium chloride side product.

Diethyl Sulfonyldicarbamate. Ethyl chloroformate (36.2 g, 0.33 mol) was added over a period of 3 h to a stirred mixture of sulfamide (12.0 g, 0.13 mol) and sodium carbonate (68.9 g, 0.65 mol) in solvent acetone (200 ml). The mixture was boiled for 18 h, allowed to cool, and then filtered. The solid residue was dissolved in 500 ml of water and the solution was acidified (pH 3) with concentrated HCl until the sulfonyldicarbamate precipitated (15.0 g, 50%). The compound was recrystallized from ethyl alcohol.

Diethyl *N,N'*-Dimethyl- d_6 -sulfonyldicarbamate. Diisopropylethylamine (8.44 g, 65 mmol) was added to a mixture of diethyl sulfonyldicarbamate (15.66 g, 65 mmol) and chloroform (50 ml). Methyl- d_3 iodide (9.45 g, 65 mmol) was added and the mixture was sealed in a thick-walled Pyrex tube. After 12 h at 55 $^\circ\text{C}$, the tube was opened and another equivalent of diisopropylethylamine (8.44 g, 65 mmol) and methyl- d_3 iodide (9.45 g, 65 mmol) was added. The reaction was run for an additional 10 h at 55 $^\circ\text{C}$ in a sealed tube. The diisopropylethylammonium iodide was extracted from the chloroform solution with water and the chloroform was removed under reduced pressure to yield diethyl *N,N'*-dimethyl- d_6 -sulfonyldicarbamate (16.1 g, 92%).

Diethyl *N,N'*-dimethylsulfonyldicarbamate was synthesized using methyl iodide as described above for the hexadeuterated compound: NMR (CDCl_3) δ 1.32 (t, 3, $J = 7.3$ Hz, CCH_3), 3.40 (s, 3, NCH_3), 4.28 (q, 2, $J = 7.3$ Hz, CH_2).

***N,N'*-Dimethyl- d_6 -sulfamide.** A solution of diethyl *N,N'*-dimethyl- d_6 -sulfonyldicarbamate (16.1 g, 60 mmol) in a methanol- d_1 (60 ml)- D_2O (15 ml) solution was refluxed under a nitrogen atmosphere with sodium methoxide (14 g, 260 mmol) for 3 h. Deuterated

solvents were used as a precaution against hydrogen exchange. The solution was acidified with DCl, the solvent removed under reduced pressure, and the product extracted with several portions of ether. The *N,N'*-dimethyl- d_6 -sulfamide (5.93 g, 69% yield based on CD_3I) was crystalline and no further attempt was made at purification.

***N,N'*-Dimethylsulfamide** was synthesized using diethyl *N,N'*-dimethylsulfonyldicarbamate as described above for the hexadeuterated compound and was identified by comparison with authentic material:²² mp 75–76 $^\circ\text{C}$; NMR (CDCl_3) δ 2.73 (s, 3, CH_3), 4.32 (s, 1, NH).

***N,N'*-Dimethyl- d_6 -hydrazine.** A solution of sodium hypochlorite in D_2O was prepared and added dropwise to a stirring solution of *N,N'*-dimethyl- d_6 -sulfamide in a D_2O solution of NaOD according to the method of Ohme for the synthesis of dimethylhydrazine.²²

Azomethane- d_6 was synthesized by HgO oxidation of *sym*-dimethylhydrazine- d_6 as described earlier for the undeuterated compound.

Diethyl *N*-Methylsulfonyldicarbamate. The monomethyl sulfonyldicarbamate was prepared by the addition of 2 equiv of benzyltrimethylammonium hydroxide (triton B, 40% solution in methyl alcohol, Aldrich Chemical Co.) to a solution of diethyl sulfonyldicarbamate in methyl alcohol. After addition of 1 equiv of methyl iodide, the mixture was sealed in a thick-walled Pyrex tube and heated to 55 $^\circ\text{C}$ for 12 h. After reaction, the mixture was acidified and the methyl alcohol removed under reduced pressure. Chloroform was added to the residue and the benzyltrimethylammonium iodide was extracted with an acidic aqueous solution. After removal of the chloroform, the diethyl *N*-methylsulfonyldicarbamate appeared as a reddish brown oil. From NMR the yield of monomethylated product was 81%: NMR (CDCl_3) δ 1.30, 1.33 (overlapping triplets, 6, $J = 7.3$ Hz, CCH_3), 3.42 (s, 2.43, NCH_3), 4.28, 4.33 (overlapping quartets, 4, $J = 7.3$ Hz, CH_2).

***N*-Benzyl-*N'*-methylsulfamide.** Diisopropylethylamine (1 equiv) and 1 equiv of benzyl chloride were added to a chloroform solution of diethyl *N*-monomethylsulfonyldicarbamate. The solution was heated to 65 $^\circ\text{C}$ under a stream of nitrogen for 12 h. The diisopropylethylammonium chloride was extracted with water, the chloroform removed under reduced pressure, and the product, diethyl *N*-benzyl-*N'*-methylsulfonyldicarbamate, was hydrolyzed to give the sulfamide, employing the same conditions used in obtaining the dimethylsulfamide: mp 105–107 $^\circ\text{C}$; NMR (acetone- d_6) δ 2.62 (s, 3, NCH_3), 4.17 (s, 2, CH_2), 7.33 (s, 5, C_6H_5).

Viscosity Measurements (at constant pressure). The viscosities of the entire range of *tert*-butyl alcohol-water mixtures were determined with a Cannon-Manning semimicro viscometer. The values of the densities used to calculate viscosities were those determined by Kenttamaa²³ and co-workers. Activation energies for viscous flow were determined from the slope of a plot of $\ln \eta$ vs. $1/T$. Viscosities were determined at four temperatures (15, 25, 40, and 50 $^\circ\text{C}$) for each solution studied (see Table I).

Viscosity Measurements (at constant volume). The viscosities at constant volume (Table II) were measured using a high-pressure rolling ball viscometer.²⁴ The roll time (t) is related to the viscosity by the following equation: $\eta = ct(\Delta\rho)$, where c is a constant and $\Delta\rho$ is the difference in density between the steel ball and the liquid.²⁵ Constant volume conditions were monitored using a high-pressure piezometer, which reflected the change in volume of the sample in the change in length of a metal bellows. The measuring circuit has been described.²⁶ For each of the *tert*-butyl alcohol-water solutions studied, the pressure required to produce at 50 $^\circ\text{C}$ a volume equal to that of the same solution at 25 $^\circ\text{C}$ and 1 atm was determined. The viscosities of the solutions at 25 $^\circ\text{C}$ and 1 atm were determined as described in the preceding section. In order to determine the calibration constant for the rolling ball viscometer each of the solutions was run at 25 $^\circ\text{C}$ and 1 atm as well as at 50 $^\circ\text{C}$ and pressure P (determined from the piezometer measurements). The activation energy of viscous flow at constant volume was determined from the slope of a plot of $\ln \eta$ (const vol) vs. $1/T$.

Results and Discussion

Synthesis. There are several widely used procedures for the synthesis of azoalkanes, but many of them give low yields, especially in the preparation of azo compounds with primary alkyl groups. Oxidative coupling of amines with iodine pentafluoride is applicable only to amines with tertiary alkyl

Table I. Viscosities (cP) and Activation Energies for Viscous Flow for *tert*-Butyl Alcohol–Water Solutions

$X_{\text{H}_2\text{O}}$	15 °C	25 °C	40 °C	50 °C	ΔH^*_{vis} , cal
1.00	1.146	0.895	0.653	0.545	4030
0.95	3.292	2.128	1.278	0.966	6779
0.90	5.032	3.232	1.812	1.337	7318
0.80	7.306	4.508	2.477	1.784	750
0.70	8.013	4.897	2.651	1.877	7926
0.50	7.957	4.844	2.570	1.799	8098
0.40	7.737	4.644	2.458	1.710	8216
0.30	7.437	4.470	2.329	1.620	8319
0.20	7.282	4.293	2.226	1.550	8492
0.10	7.457	4.280	2.138	1.468	8951
0.05	7.799	4.319	2.131	1.459	9296
0.00		4.484	2.115	1.418	9650

Table II. Viscosities (cP) and Activation Energies of Viscous Flow (cal) at Constant Volume for *tert*-Butyl Alcohol–Water Solutions^a

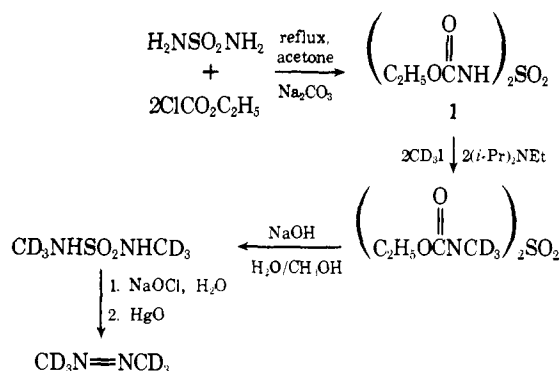
$X_{\text{H}_2\text{O}}$	Density, g cm ⁻³	$\eta_{25\text{ °C}}$ (1 atm)	$\eta_{50\text{ °C}}$ (P atm)	$(\Delta H^*_{\text{vis}})_{\text{vol}}$
1.00	0.9971	0.895	0554 (235)	3619
0.95	0.9695	2.128	1.031 (415)	5852
0.90	0.9425	3.232	1.461 (435)	6382
0.80	0.8963	4.508	2.136 (397)	6022
0.50	0.8266	4.844	2.452 (305)	5517
0.20	0.7941	4.293	2.407 (290)	4735
0.05	0.7835	4.319	2.264 (265)	5249

^a The pressure was adjusted to make the density at 50 °C equal to that at 25 °C for each solvent mixture.

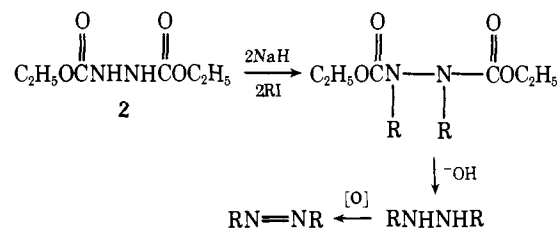
groups.^{27–29} Oxidation of *N,N'*-dialkylhydrazines, prepared by condensation of hydrazine with an aldehyde or ketone followed by reduction of the carbon–nitrogen double bond,³⁰ is a method which is applicable to azo compounds with primary or secondary alkyl groups. Unfortunately, the azine $\text{CH}_2=\text{NN}=\text{CH}_2$ cannot be obtained from formaldehyde and hydrazine.²⁰

The hypochlorite oxidation of sulfamides to give azoalkanes^{31,32} has recently been developed as a synthesis of unsymmetrical aryl-*tert*-alkyl azo compounds,³³ as has the analogous oxidation of *N*-aryl-*N'*-*tert*-alkylureas.³⁴

Although the formation of *N,N'*-dimethylhydrazine from the corresponding sulfamide proceeds in 95% yield, only a 25% yield of the starting *N,N'*-dimethylsulfamide is obtained from methyl amine in the reaction with sulfuryl chloride and pyridine. This led us to develop a new method for the synthesis of azoalkanes based on the alkylations of diethyl sulfonyldicarbamate (**1**) as illustrated in Scheme I, a method with greatly enhanced efficiency in the conversion of primary amine to azoalkane.

Scheme I

The pictured preparation of **1** from sulfamide²¹ proved to be more convenient than the literature method,³⁵ which involved the reaction of silver cyanate and chlorosulfonyl isocyanate. The dialkylation of **1**, with weak base catalysis, leads to a high yield of symmetrical dialkyl hydrazines. This route is similar to that employed by Al-Sader and Crawford³⁶ for the synthesis of azoalkanes, including several unsymmetrical ones, by two successive alkylation steps.



Attempted monoalkylations of **1** using weak base catalysts gave mixtures of unsubstituted, monoalkylated, and dialkylated products, leading to problems in separations and lowered yields of monoalkylated material, observations parallel to those reported⁶ for alkylations of **2**. The synthesis of Scheme I is easily modified to provide high yields of monoalkylation. The acidity of **1** is high enough that the dianion is easily formed by treatment with 2 equiv of triton B in methanol. The greater nucleophilicity of the dianion thus generated, relative to the monoanionic alkylation product, allows one cleanly to form monoalkylated product from 1 equiv of alkylating agent. Addition of 1 equiv of a second alkylating agent can then lead to the desired precursor of the unsymmetrical azoalkane. Evidence was obtained by NMR spectroscopy for the formation in high yield of the unsymmetrical compound *N*-benzyl-*N'*-methylsulfamide from successive alkylations of **1**, followed by hydrolysis.

Cage Recombination in the Photolysis of Azomethane.

Equation 10 has been derived to correlate data from studies of cage reactions with properties of the solvent in which the reactions are run. The phenomenon of cage combination is observed in systems involving two radicals simultaneously produced in solution. The geminate pair of radicals may either combine to give a dimer or diffuse apart into the bulk of the solution to give free radicals. The presence of suitable scavengers will prevent the subsequent combination of these free radicals. In such systems the dimer results from cage reaction only. It is often assumed that k_c , the rate constant for combination of caged radical pairs, is independent of solvent and that all the variation in cage product may be attributed to k_d , the effective rate constant for diffusion from the cage. Several workers have studied the effects of the solvent medium on the geminate recombination of paired radicals and have derived equations relating the rate constant for diffusive separation of a radical pair to various powers of the fluidity ($1/\eta$). In this work, k_d will be taken as directly proportional to the diffusion

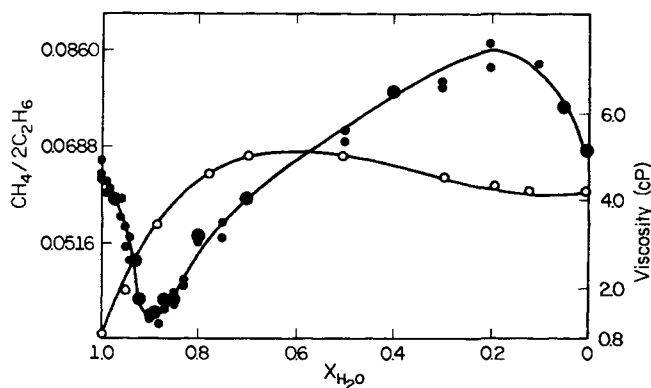
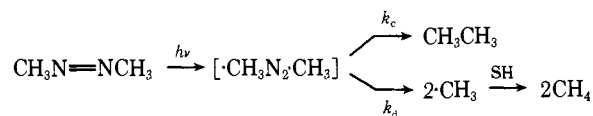


Figure 1. Cage effects in the photodecomposition of azomethane (closed circles) and viscosities (open circles) in aqueous *tert*-butyl alcohol solutions at 25 °C. Larger dots represent two identical data points. Data are from Table III.

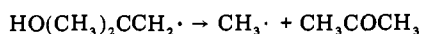
coefficient (D). We have not applied eq 10 to solvents with a wide enough range of fluidities to allow the choice of an appropriate power dependence on D to be made. In correlating cage effects with solvent properties, values of k_d/k_c for a particular radical initiator, $\text{CH}_4/2\text{C}_2\text{H}_6$ in the case of azomethane, are therefore plotted against $c(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$ (as demanded by eq 10, to be discussed later).

Azomethane was photolyzed at 25 °C in a series of aqueous *tert*-butyl alcohol solutions. A number of physical properties of highly aqueous binary solvents as well as enthalpies of activation of many solvolysis reactions in these solvents exhibit extrema at about 0.9 mol fraction of water (0.9 $X_{\text{H}_2\text{O}}$). For aqueous solutions of the lower alcohols, the extrema become larger and occur at higher mole fractions of water as the size of the alcohol molecule is increased. Highly aqueous *tert*-butyl alcohol solutions have given the largest extrema of this kind. In Figure 1 and Table III it is indeed observed that the $\text{CH}_4/2\text{C}_2\text{H}_6$ ratio produced from azomethane decomposition exhibits a sharp minimum at 0.9 mol fraction of water. The following scheme illustrates that the ratio $\text{CH}_4/2\text{C}_2\text{H}_6$ may be equated to k_d/k_c and is thus a measure of the rate of diffusion of methyl radicals from the cage relative to recombination, a process assumed to be solvent independent. In this scheme, SH represents a solvent molecule with an abstractable hydrogen.



Kharasch, Rowe, and Urry³⁷ examined the methane obtained from the decomposition of acetyl peroxide at 80 °C in *tert*-butyl alcohol, which was deuterated to the extent of 7.43 mol % in the hydroxyl group. The methane was isotopically normal, within the limits of detection of their experiment, leading to the conclusion that methyl radicals abstracted hydrogen atoms from the methyl group of *tert*-butyl alcohol rather than from the hydroxyl group.³⁸

The α -hydroxyalkyl radicals formed by hydrogen abstraction from the methyl groups of *tert*-butyl alcohol either recombined or fragmented to give an alternative source of methyl radicals which must be considered in the present work.



At 80 °C in *tert*-butyl alcohol the acetone-methane ratio was only 0.028, suggesting that the pictured source of methyl radical, and hence methane, was unimportant relative to that giving methyl radicals from the initiator.³⁸ At 25 °C, the

Table III. Diffusion Parameters and Cage Effects for the Photodecomposition of Azomethane in Alcohol-Water Solutions at 25 °C

$X_{\text{H}_2\text{O}}$	$10^3(\text{CH}_4/2\text{C}_2\text{H}_6)^a$	$10^4 c(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1},$ $\text{cal}^{-1} \text{ml}^{1/3} \text{g}^{1/2}$
Aqueous <i>tert</i> -Butyl Alcohol		
1.00	63, 64, 66	1.14
0.99	60, 62	
0.98	60, 61	
0.97	59, 59	
0.96	59, 56	
0.95	54, 51	0.80
0.94	52, 48	
0.93	48, 48	
0.92	41, 41	
0.90	39, 38	0.75
0.89	39, 39	
0.88	37	
0.87	40, 41, 41	
0.85	41, 41, 40, 42	
0.83	44, 45	
0.80	52, 52, 52	0.95
0.75	52, 55	
0.70	59, 59	1.05
0.50	70, 71	1.15
0.40	78, 78	1.31
0.30	79, 80	
0.20	87, 83	1.43
0.10	83	
0.05	74, 74	
0.0	68, 68	1.30
Aqueous Methanol		
1.00	63, 64, 66	1.14
0.99	64	
0.90	71, 74	
0.87		1.07
0.80	73, 72	
0.70	77, 78	
0.66		1.18
0.60	83, 85	
0.50	100, 101	
0.41		1.75
0.30	145, 150	
0.0	194, 202	2.90

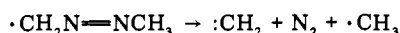
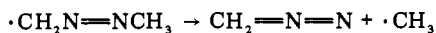
^a Multiple entries in this column are results of duplicate runs.

temperature for most of our studies, the fragmentation of the α -hydroxyalkyl radical would be expected to be even less important, justifying our ignoring this possible source of methane.

It has been assumed in the above scheme that all the measured ethane is cage product; however, this may not necessarily be the case for decompositions in highly aqueous *tert*-butyl alcohol media. Water is a very poor hydrogen-atom donor³⁸ and *tert*-butyl alcohol is an inferior hydrogen-atom donor, since it contains only primary alkyl C-H bonds. Methyl radicals that have escaped the solvent cage might therefore live long enough to recombine with a second free methyl radical. To determine whether or not noncage ethane is formed, roughly equimolar amounts of azomethane and azomethane- d_6 were decomposed in 90 and 99 mol % aqueous *tert*-butyl alcohol solutions (0.9 and 0.99 $X_{\text{H}_2\text{O}}$). The photolysis of the azomethane-azomethane- d_6 mixture in 0.99 $X_{\text{H}_2\text{O}}$ revealed no more than 0.7% of the ethane to be CH_3CD_3 , arising from random combination of free methyl radicals outside the solvent cage. This reflects a random combination of no more than 1.5% of the methyl radicals generated. The photolysis of the azomethane mixture in 0.90 $X_{\text{H}_2\text{O}}$ medium resulted in the formation of no detectable cross-labeled ethane. The results of

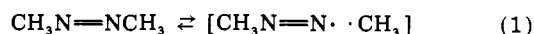
these experiments are therefore consistent with the assumption that the ratio $\text{CH}_4/2\text{C}_2\text{H}_6$ is equal to k_d/k_c in 0.90 $X_{\text{H}_2\text{O}}$ and suggest that the assumption is valid within experimental error, even in 0.99 $X_{\text{H}_2\text{O}}$ media.

Consideration should also be given to the possibility of hydrogen abstraction from an azomethane molecule by a methyl radical. Since more methane is observed in pure water (a poor hydrogen atom donor) than in solutions containing a few mol percent of *tert*-butyl alcohol (a better hydrogen-atom donor) it appears that azomethane might well be donating hydrogen atoms to methyl radicals in 100% aqueous solution. The following modes of decomposition of the radical $\cdot\text{CH}_2\text{N}=\text{NCH}_3$ can be imagined.

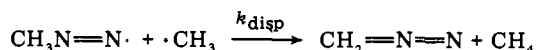


Either of these reactions might produce noncaged methyl radicals in a chain process. However, the chain length might be expected to be short, since the chain process involves the resonance stabilized $\cdot\text{CH}_2\text{N}_2\text{CH}_3$ radical. Rebert and Aulsloos³⁹ studied photolyses of equimolar mixtures of azomethane and azomethane-*d*₆ in the neat liquid, where the only hydrogen source is azomethane itself. Under these conditions, it was found that the ratio $\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$ is approximately equal to the ratio $(\text{CH}_4 + \text{CH}_3\text{D})/(\text{CD}_3\text{H} + \text{CD}_4)$. For either $\text{CH}_3\cdot$ or $\text{CD}_3\cdot$, the value k_H/k_D was proved to be ca. 4. If the chain process producing unpaired methyl radicals from $\cdot\text{CH}_2\text{N}=\text{NCH}_3$ or $\cdot\text{CD}_2\text{N}=\text{NCD}_3$ were taking place to a significant extent, then the ratio $(\text{CH}_4 + \text{CH}_3\text{D})/(\text{CD}_3\text{H} + \text{CD}_4)$ should, in fact, be greater than $\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$, and this was not observed.

In gas-phase photolyses of azomethane it is well established that the quantum yield for nitrogen production is unity from 298 to 473 K. This indicates that under these conditions the $\text{CH}_3\text{N}=\text{N}\cdot$ radical, if formed, decomposes before it has a chance to recombine with another radical or to react with an azomethane molecule. The fact that the quantum yield of nitrogen is lower than 0.1 in liquid-phase photolysis may be explained by the cage recombination reaction illustrated below.



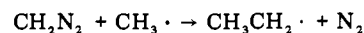
An alternative explanation could be based on the recent suggestion by Porter³³ that photolysis of an azo compound occurs by photoisomerization to the *cis* isomer, which then decomposes to radical products by a thermal process. In this scheme solvent could facilitate a thermal reversion to the stable *trans* isomer, thus lowering the quantum yield for decomposition of the azo compound. If $\text{CH}_3\cdot$ and $\text{CH}_3\text{N}_2\cdot$ are formed as a radical pair, disproportionation could yield diazomethane and methane. In this reaction methane is a cage product. If the product ratio $(\text{CH}_4/)\text{C}_2\text{H}_6$ is to be taken equal to k_d/k_c , then a correction would have to be made to take into account the "cage" methane if this reaction were important.



To assess the importance of "cage" methane, an equimolar mixture of azomethane and azomethane-*d*₆ was photolyzed in CCl_4 at 0 °C. Methyl chloride is the major noncage product, formed by chlorine-atom abstraction from CCl_4 by free methyl radicals. Methane, also formed in the reaction, may be attributed to either hydrogen abstraction from azomethane (0.05 M) or a cage disproportionation reaction. If a significant portion of the methane were produced as a cage product, the methane should consist to that degree of CH_4 and CD_4 . Any CD_3H or CH_3D observed must be formed by a noncage process. Mass spectrometric analysis of the product, methyl chloride, at 10 eV shows that the ratio $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl}$ is equal

to about 1.37. A similar value, 1.41, is found for the $\text{CH}_3\text{D}/\text{CD}_4$ ratio. Since both methyl chloride and CH_3D are formed from free methyl radicals, the above results suggest that CD_4 is also formed from free methyl radicals in a noncage process.

The isotopic composition of the ethane determined in the isotopic tracer experiments can be used to rule out significant contributions from the reaction pathway leading to ethane by reaction of diazomethane with free methyl radicals.



Loss of free methyl radicals in reactions other than hydrogen-atom abstractions has not been considered in the above discussions. The fact that in the aqueous media of the labeling study CH_3CD_3 is a very minor product does not necessarily rule out reactions of methyl radicals with more stable radicals in solution. Also, addition of methyl radicals to azomethane, giving trimethyl hydrazyl radicals, may result in loss of methyl radicals. Failure to take these reactions into account would lead to too small values of k_d/k_c as measured by $\text{CH}_4/2\text{C}_2\text{H}_6$. The effect should be greater in pure water than in 90% aqueous *tert*-butyl alcohol, since the addition of a hydrogen donor will result in an increase in the scavenging of methyl radicals to give methane. The net result would be an even more pronounced minimum in k_d/k_c at 90% water than is seen in Figure 1.

Although we did not do quantitative experiments to assess the importance of this mode of loss of methyl radicals, the GLC analyses of reaction mixtures showed no appreciable variation of methane yield with composition of the medium as judged by methane peak area at constant instrument settings. This reaction is not an important one.

Correlation of Cage Effects with Macroscopic Solvent Parameters. In many studies, reasonably successful correlations have been established between cage effects and various functions of the viscosity of the medium (*vide supra*). The viscosities of the entire range of *tert*-butyl alcohol-water mixtures of this study were measured and the results are plotted in Figure 1 along with the cage effect data. The solvent dependence of viscosity for this binary solvent system does not parallel the complex solvent dependence of k_d/k_c for azomethane decomposition in this same media. In particular, the minimum in k_d/k_c which occurs at 0.90 $X_{\text{H}_2\text{O}}$ does not correspond to the solvent composition for maximal viscosity (about 0.60 $X_{\text{H}_2\text{O}}$). Thus, in the region $0.90 > X_{\text{H}_2\text{O}} > 0.60$, the viscosity is increasing in magnitude while the cage effect is decreasing. This trend is contrary to that usually observed in organic solvents.⁴⁰ MacDonald and Hyne have shown that the internal pressure exhibits a sharp extremum in the high water region of aqueous *tert*-butyl alcohol mixtures.^{41a} Arnett and Hufford have observed that the energy of an electronic transition of a certain dye goes through an extreme in this same region of solvent composition.^{41b,c} The solvent dependence of the cage effect appears to be more closely parallel to the latter two observations than to the dependency of viscosity on solvent composition.

In order to test the correlation of k_d/k_c with eq 10, the equation describing the diffusion coefficient, which is developed later in this paper, values were needed for $(\Delta H^*_{\text{vis}})_p$, the enthalpy of activation for viscous flow at constant pressure, and $(\Delta H^*_{\text{vis}})_{\text{vol}}$, the enthalpy of activation for viscous flow at constant volume. Determination of values for these quantities for aqueous *tert*-butyl alcohol solutions allowed us to determine values for two quantities used in eq 10, P_{eff} , the effective pressure, and c , the lattice factor (*vide infra*). Values for the internal pressure (P_i)⁴² and the cohesive energy density (P_c) needed for the correlation were obtained from literature sources.

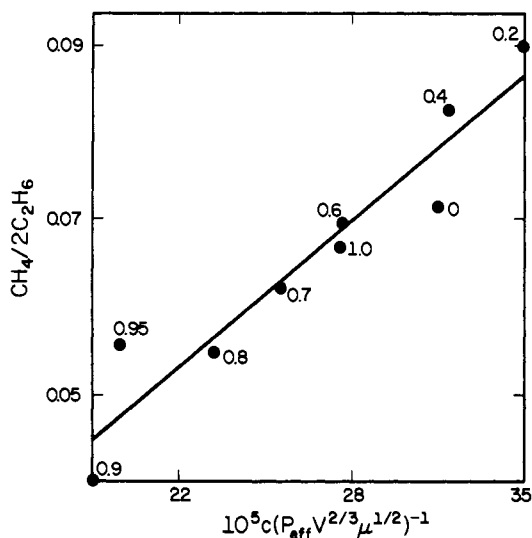


Figure 2. Photolyses of azomethane in aqueous *tert*-butyl alcohol solutions. The mole fraction of water is indicated by each point ($r = 0.953$). Data are from Table III.

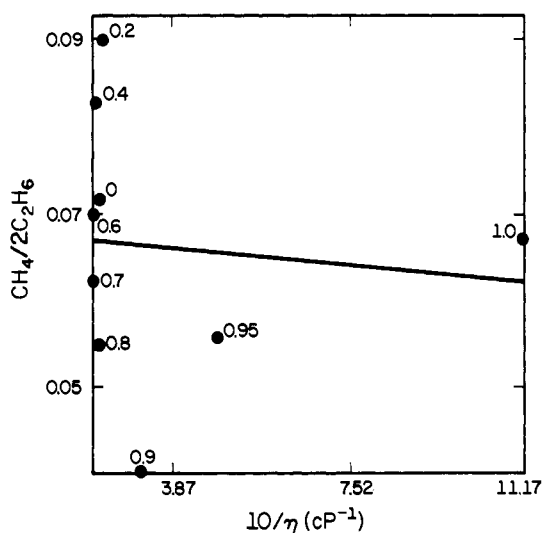


Figure 3. Azomethane decomposition in aqueous *tert*-butyl alcohol solutions. The mole fraction of water is indicated by each point ($r = 0.106$). Data are from Table III.

A plot of $(\Delta H^*_{vis})_p$ vs. X_{H_2O} is presented in Figure 11 (in the microfilm edition). Throughout the entire range of solutions, from 100% water to 100% *tert*-butyl alcohol, $(\Delta H^*_{vis})_p$ is a continuously increasing function. Although no extremum is exhibited, it is interesting to note that the regions of the greatest rate of increase (between 100 and 90%; and between 20 and 0% water) correspond to the same regions in which the cage effect is increasing (i.e., k_d/k_c is decreasing). It has been suggested⁴³ that the energy of activation for the elementary flow process is some fraction of the energy of vaporization. In Figure 12 (in the microfilm edition) a plot of E_{vap} vs. X_{H_2O} shows that, while the energy of viscous flow may not be a constant fraction of the energy of vaporization over the whole range of compositions, the overall shapes of the two curves are quite similar. A plot of $(\Delta H^*_{vis})_{vol}$ vs. X_{H_2O} is shown in Figure 13 (in the microfilm edition). Unlike $(\Delta H^*_{vis})_p$ or the viscosity, $(\Delta H^*_{vis})_{vol}$ exhibits a maximum value at $X_{H_2O} 0.90$, suggesting that it is a structure-sensitive solvent parameter.

A plot of our solvent parameter $c(P_{eff}V^{2/3}\mu^{1/2})^{-1}$ vs. X_{H_2O} exhibits a minimum at $X_{H_2O} 0.90$ and a maximum at X_{H_2O}

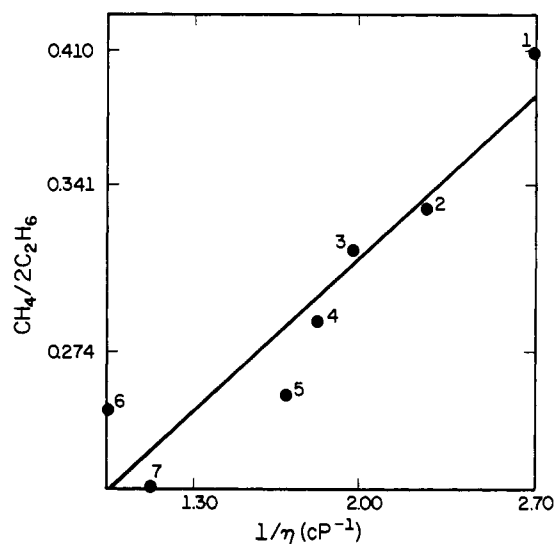


Figure 4. Azomethane decomposition at 25 °C. Solvents: 1, hexane; 2, ethylacetate; 3, *n*-octane; 4, toluene; 5, benzene; 6, ethanol; 7, cyclohexane ($r = 0.937$), data of ref 41.

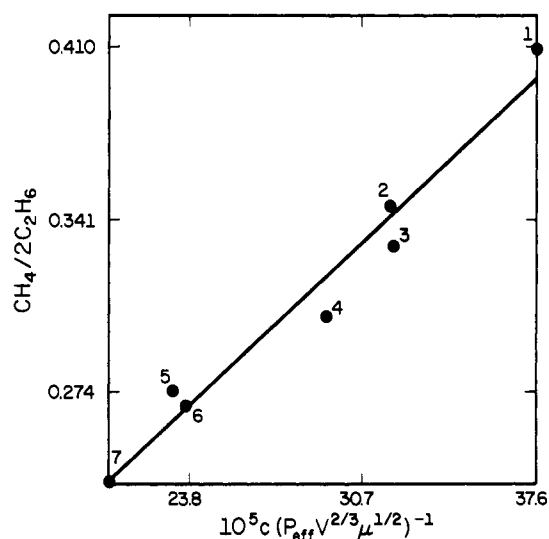


Figure 5. Azomethane decomposition at 25 °C. Solvents: 1, hexane; 2, ethyl acetate; 3, *n*-octane; 4, toluene; 5, benzene; 6, ethanol; 7, cyclohexane ($r = 0.982$), data of ref 41.

0.20 with a detailed solvent dependence remarkably similar to that shown for the ratio $CH_4/2C_2H_6$ in Figure 1. In Figure 2 (Table III) a plot of $CH_4/2C_2H_6$ vs. $c(P_{eff}V^{2/3}\mu^{1/2})^{-1}$ exhibits a correlation coefficient of 0.953. On the other hand, a plot of $CH_4/2C_2H_6$ vs. $1/\eta$ shows almost no correlation ($r = 0.106$) in Figure 3. It is not surprising that a better correlation is seen using an expression involving four experimentally determined solvent parameters, but the form of the dependence is instructive.

Kodama⁴⁴ has photolyzed azomethane in a number of solvents and pointed out that the yield of ethane shows a fairly good correlation with the viscosity of the solvent. A plot of the k_d/k_c ratio (from Kodama's study) vs. the fluidity gives a correlation coefficient (r) of 0.937 (Figure 4). In Figure 5, the same cage effect data are plotted against $c(P_{eff}V^{2/3}\mu^{1/2})^{-1}$, with $r = 0.982$.

Extrema of many physical properties occur at much lower mole fraction of the organic cosolvent in *tert*-butyl alcohol-water mixtures than in methanol-water mixtures. In addition, the sizes of the extrema in methanol-water are generally the

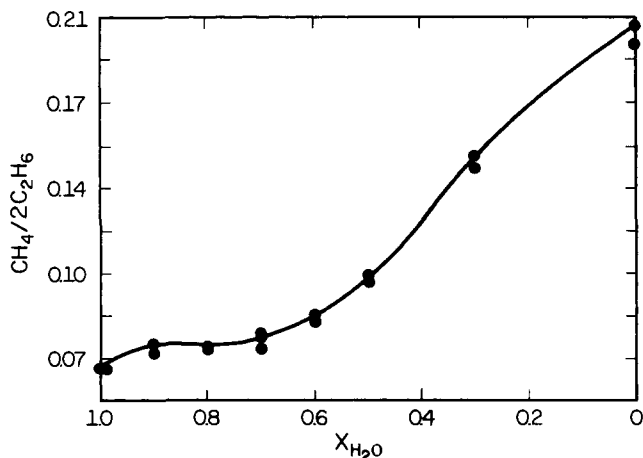


Figure 6. Cage effects in the photodecomposition of azomethane at 25 °C in aqueous methanol. Data are from Table III.

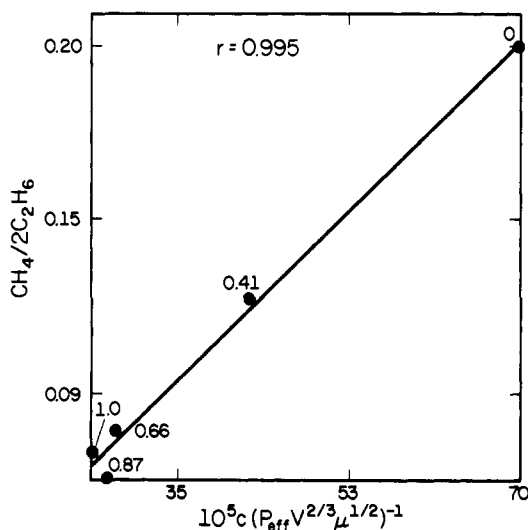


Figure 7. Azomethane decomposition in aqueous methanol at 25 °C. The mole fraction of water is indicated by each point. Data are from Table III.

smallest of all the simple alcohol-water solutions. In analogy to these properties of methanol-water mixtures, a shallow minimum in k_d/k_c at around 70% water was expected and found for the photodecomposition of azomethane in these solutions. As seen in Figure 6, between 100 and 70% water the methane/ethane ratio is observed to be fairly constant. At 70% water, $\text{CH}_4/2\text{C}_2\text{H}_6$ begins to rise sharply until the value is more than doubled in pure methyl alcohol. In order to correlate the cage effect data with eq 10, $(\Delta H^*_{\text{vis}})_p$ and $(\Delta H^*_{\text{vis}})_{\text{vol}}$ must be known for the whole range of methyl alcohol-water mixtures. Although values for $(\Delta H^*_{\text{vis}})_p$ are available in the literature, $(\Delta H^*_{\text{vis}})_{\text{vol}}$ is available only for 100% water and 100% methyl alcohol. From the behavior of the ratio $(\Delta H^*_{\text{vis}})_{\text{vol}}/(\Delta H^*_{\text{vis}})_p$ (the parameter n in eq 15) for *tert*-butyl alcohol-water solutions, reasonable values of the ratio and hence $(\Delta H^*_{\text{vis}})_{\text{vol}}$ were estimated for methanol-water mixtures. (In aqueous *tert*-butyl alcohol mixtures the region between 100 and 90% water is an essentially aqueous region where the three-dimensional tetrahedral water structure is present. This region is characterized by increasing internal pressures with increasing temperature. For *tert*-butyl alcohol-water, the ratio $(\Delta H^*_{\text{vis}})_{\text{vol}}/(\Delta H^*_{\text{vis}})_p$ is fairly constant in this region, decreasing slightly from 0.90 to 0.87 from pure water to 90% water. Between 90 and 0% water, the tetrahedral water structure is essentially destroyed and the entire region is

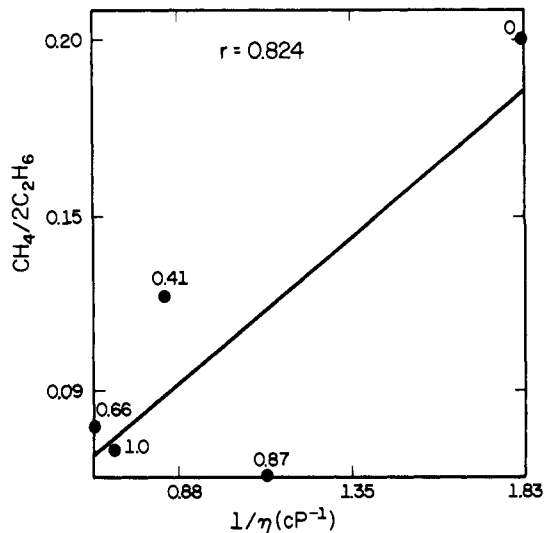


Figure 8. Azomethane decomposition in aqueous methanol at 25 °C. The mole fraction of water is indicated by each point. Data are from Table III.

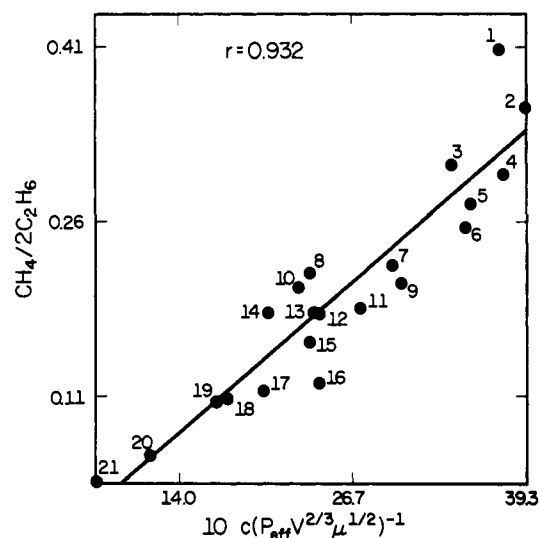


Figure 9. Azomethane decomposition at 20 °C (data from Table IV). Solvents: 1, ethyl ether; 2, pentane; 3, CH_2Cl_2 ; 4, hexane; 5, acetonitrile; 6, heptane; 7, methanol; 8, ethanol; 9, nonane; 10, CCl_4 ; 11, decane; 12, ethylene dichloride; 13, 1-propanol; 14, cyclohexane; 15, 1-butanol; 16, dodecane; 17, Me_2SO ; 18, cyclohexanone; 19, dioxane; 20, water; 21, 90% water-10% *tert*-butyl alcohol.

characterized by slightly decreasing internal pressures with increasing temperatures. In this region, the ratio decreases linearly from 0.87 at 90% water to 0.56 in 0% water. For aqueous methanol, the "aqueous" region, characterized by increasing internal pressures with increasing temperature, lies between 100 and 70% water. In this region it was assumed the $(\Delta H^*_{\text{vis}})_{\text{vol}}/(\Delta H^*_{\text{vis}})_p$ varies linearly from 0.90 to 0.87. In the region between 70 and 0% water, the ratio was assumed to vary linearly from 0.87 to 0.66, the known value for pure methyl alcohol.) Using the above assumptions to calculate $c(P_{\text{eff}} V^{2/3} \mu^{1/2})^{-1}$ for the methyl alcohol-water system, a good correlation, $r = 0.995$, of the cage effect (Table III) with the diffusion equation (eq 10) was found (Figure 7). In contrast, a plot of k_d/k_c vs. $1/\eta$ shows $r = 0.824$ (Figure 8).

Cage effects in azomethane decompositions were also studied in 21 different pure solvents (Table IV) including alcohols, hydrocarbons, chlorocarbons, ethers, sulfoxides, ketones, etc. A plot of these data vs. our diffusion parameter (Figure 9) shows $r = 0.932$, while a plot vs. $1/\eta$ has an r of 0.890 (Figure 10).

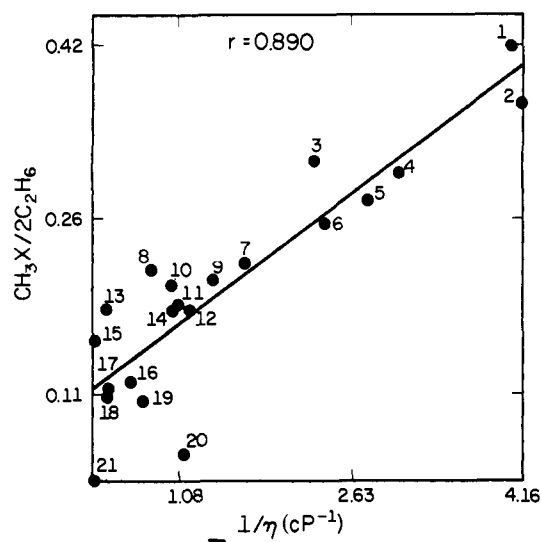
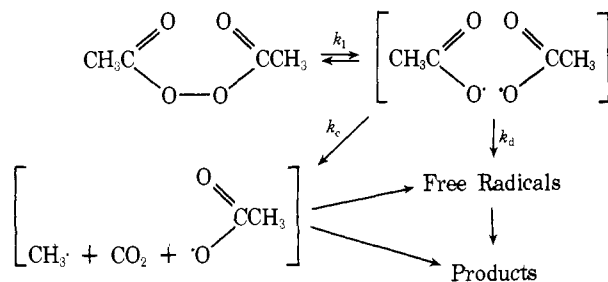


Figure 10. Azomethane decomposition at 20 °C. See Figure 9 for identification of solvents.

The cage effect⁴⁵ in the photolytic generation of trifluoromethyl radicals from perfluoroazomethane ($\text{CF}_3\text{N}_2\text{CF}_3$) at 65 °C is correlated ($r = 0.942$) with values of $(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$ at 20 °C for the 18 solvents for which appropriate experimental data were available for the calculation of our solvent parameter.

The most generally accepted mechanism^{46,47} for decomposition of acetyl peroxide is given by Scheme II.

Scheme II



The kinetic data of Pryor and Smith⁵ for the decomposition of acetyl peroxide at 80 °C in normal alkane solvents are correlated with $c(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$ with $r = 0.990$.

Activation volumes have been shown⁴⁸ to be positive for decompositions of a variety of radical initiators in accord with the simple idea that homolytic bond scission is characterized by an increase in volume upon going to the transition state. It is interesting that the rate constants for decomposition of azocumene at 55 °C in a range of solvents show no correlation with solvent internal pressure,^{48a} but are correlated with the diffusion parameter of eq 10, $c(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$, with an r of 0.801.

Development of the Equation for the Diffusion Coefficient. The theory of diffusion in the liquid state has been approached historically from two quite different directions. According to an older model due to Eyring,⁴⁹ diffusion of a molecule occurs by jumps of about one molecular diameter from a solvent lattice position into a neighboring hole or vacancy by an activated process. According to the more recent models,^{50,51} thermal diffusion of molecules occurs by random walk processes involving displacements small compared to molecular diameters.

There has been considerable success in treating properties of certain liquids in terms of theoretical models involving

Table IV. Diffusion Parameters and Cage Effects for the Photodecomposition of Azomethane in 19 Solvents at 20 °C

Solvent	$10^3(\text{CH}_4/2\text{C}_2\text{H}_6)^a$	$10^4c(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$, cal ⁻¹ ml ^{1/3} g ^{-1/2}
Ethyl ether	420	3.74
<i>n</i> -Pentane	368	3.93
CH_2Cl_2	318 ^b	3.38
<i>n</i> -Hexane	309	3.76
Acetonitrile	285	3.53
<i>n</i> -Heptane	264	3.48
Methanol	230	2.94
Ethanol	224	2.35
CCl_4	211 ^b	2.26
<i>n</i> -Nonane	215	3.01
<i>n</i> -Decane	194	2.77
1,2-Dichloroethane	189 ^b	2.40
1-Propanol	189	2.38
1-Butanol	163	2.34
Cyclohexane	188	2.03
<i>n</i> -Dodecane	126	2.41
Dimethyl sulfoxide	120	2.00
<i>p</i> -Dioxane	110	1.66
Cyclohexanone	113	1.75

^a Average of at least two determinations. ^b Values of $(\text{CH}_4 + \text{CH}_3\text{Cl})/2\text{C}_2\text{H}_6$ are reported.

hard-sphere molecules.^{50a,51} For a solute molecule such as the methyl radical, which is not expected to show important specific interactions with hydrogen-bonding solvents, we can view the motions of the solute molecules, even in associated solvents, in very similar terms and develop a model for diffusion starting from kinetic gas theory.

Elementary diffusion theory⁵² suggests a diffusion coefficient (D) for gases described by

$$D = k\lambda v \quad (2)$$

where λ is the mean free path, v is the mean molecular velocity, and k is a constant with a value of approximately 0.6. In developing equations to treat the diffusion of solute molecules in the liquid phase, the mean free path of a molecule, being much smaller than the distance between neighboring sites, will be considered to be equal to the cube root of the free volume⁵³ of the liquid, $V_F^{1/3}$. By analogy to eq 2 we can write

$$D_{\text{liq}} = 0.6V_F^{1/3}v \quad (3)$$

Within the framework of assumptions which we have adopted we can use simple kinetic theory⁵⁴ to write an equation of state

$$[P + (\partial E/\partial V)_T]V^{2/3}V_F^{1/3} = cRT \quad (4)$$

where V is the total volume of the system, P is the external pressure applied to the system, and $c = 2$ for a cubic closest packing arrangement of molecules in a unit cell of the liquid. The lattice factor (c) will not necessarily equal two for other types of packing and may vary with temperature.

The work done when a perfect gas is compressed isothermally from a volume V_{gas} to a volume V_{liq} is equal to the latent heat of vaporization. In eq 4, the pressure acting on a molecule is the sum of the forces of mutual attractions of the molecules (the internal pressure P_i or $(\partial E/\partial V)_T$) and the external pressure (P). In the case of an ideal gas, the internal pressure is zero, since intermolecular forces are absent. In the case of an imperfect gas, $(\partial E/\partial V)_T$ becomes appreciable, and in the case of a liquid it may become much greater than the external pressure, with typical values lying between 2000 and 5000 atm. Thus at 1 atm the external pressure (P) can be neglected in comparison with P_i so that eq 4 becomes

$$P_1 V^{2/3} V_F^{1/3} = cRT \quad (5)$$

From eq 3, the expression for the diffusion coefficient of a liquid molecule may now be written as

$$D = 0.6 \frac{cRTv}{P_1 V^{2/3}} \quad (6)$$

In a liquid in which diffusive displacements of solvent molecules are truly random, the average velocity is given⁴ by

$$v = (8RT/\pi M)^{1/2} \quad (7)$$

where M is the molecular weight of the solvent. Thus eq 6 becomes

$$D = 0.96 \frac{c(RT)^{3/2}}{P_1 V^{2/3} M^{1/2}} \quad (8)$$

In the Appendix we outline the justifications used to develop eq 8 into the more generally useful

$$D = 0.96 \frac{c(RT)^{3/2}}{P_{\text{eff}} V^{2/3} \mu^{1/2}} \quad (9)$$

where P_{eff} is an "effective pressure" calculated from P_c , the cohesive energy density ($\Delta E_{\text{vap}}/V$), and internal pressure P_i , using an independently determined mixing coefficient, and μ is the reduced mass appropriate for relative diffusion of solvent and solute molecules.⁵²

At constant temperature a quantity proportional to the rate of diffusion of a particular pair of radicals from the solvent cage ($(k_d)_{\text{rel}}$), assumed to be proportional to D , is given by

$$(k_d)_{\text{rel}} \propto c(P_{\text{eff}} V^{2/3} \mu^{1/2})^{-1} \quad (10)$$

Our goal was to determine values for all of the factors in eq 10 from independent measurements of macroscopic solvent properties and use these to obtain satisfactory correlations of data bearing on the solvent cage effect in the decomposition of radical initiators in a wide range of solvent types. We were guided in our formulation of eq 10 by efforts to obtain a satisfactory fit for the complex dependence of cage recombination of methyl radicals from azomethane on solvent composition in aqueous *tert*-butyl alcohol (Figure 1). In the Appendix we detail considerations used in deriving (a) the form of P_{eff} (which determines the effective free volume available to a diffusing molecule), (b) the value of c , the lattice parameter (which is derived from measurements of activation enthalpies for viscous flow at constant volume), and (c) the effective molecular weight of water. In a number of semiempirical studies of solvent properties for highly associated solvents it has been found necessary to invoke the idea of an effective molecular weight for molecules which are extensively associated by hydrogen bonding. The Appendix discusses considerations leading to our choice of an effective molecular weight for water 2.6-fold larger than its formula weight, in effect a disposable parameter in this treatment, but one with a literature precedent.

Conclusion

With the objective of correlating the relative rates of diffusion of methyl radical pairs from the solvent cage with macroscopic solvent parameters, we have derived a semiempirical diffusion equation (eq 10) which is useful over a wide range of solvent types, including the entire range of aqueous *tert*-butyl alcohol solvents. Application of the equation requires a knowledge of several experimentally determinable solvent parameters: the internal pressure (P_i), the cohesive energy density (P_c), the activation energy for viscous flow ($(\Delta H^*_{\text{vis}})_p$), and the activation energy for viscous flow at constant volume ($(\Delta H^*_{\text{vis}})_{\text{vol}}$).

In the picture of the diffusion process upon which this treatment is based a molecule is considered to be oscillating in a "cage" composed of neighboring molecules. The free

volume available for this oscillation controls the frequency of collisions between the diffusing molecules and solvent molecules and is thus a determinant of the rate of diffusion. The free volume is related to the attractive forces between solvent molecules reflected in P_i and P_c . In a hydrogen-bonding medium the solute is surrounded not by a shell of rigid hydrogen bonds but by a flexible envelope of variable surface area. Since the hydrogen-bond network is flexible, only a fraction of its total cohesive energy (reflected in P_c) contributes to the effective free volume of the liquid, while all of the cohesive energy related to the dispersion forces (reflected in P_i) contributes. The minimum in the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio in aqueous *tert*-butyl alcohol at 0.9 $X_{\text{H}_2\text{O}}$ (Figure 1) results in part from the stiffening of the hydrogen-bond network at this solvent composition, which results in a greater fractional contribution of the cohesive energy of the hydrogen bonds—a greater P_{eff} resulting in a smaller effective free volume and slower diffusion.

The correlation equation is expected to allow the prediction of relative rates of diffusion from the cage for radical pairs, such as the nonpolar methyl radical pairs of this study, in which specific solvation is unimportant. It will be most useful in treating associated liquids, where viscosity correlations often do not hold.

Acknowledgment. This work was supported by a grant, CE 13963, from the National Institutes of Health and, in part, by grants CA 11388 and GM 16864 for the purchase of instrumentation for mass spectrometry. We wish to thank Professors David Chandler and Jiri Jones for helpful discussions and Professor Jonas for allowing us to use apparatus designed and constructed in his laboratory for the measurements of $(\Delta H^*_{\text{vis}})_{\text{vol}}$.

Appendix

The value of the internal pressure is experimentally accessible as the difference between the thermal pressure term ($T(\partial P/\partial T)_v$) and the external pressure. The isochoric thermal pressure coefficient ($(\partial P/\partial T)_v$) is directly accessible from the determination of isochoric P vs. T plots. A closely related property, the cohesive energy density (P_c), is expressed in

$$P_c = \Delta E_{\text{vap}}/V \quad (11)$$

where ΔE_{vap} is the energy of vaporization. The cohesive energy density and the internal pressure are approximately equal in magnitude for most nonpolar liquids.⁵⁶ In the case of hydrogen-bonding liquids, however, the cohesive energy density is much greater than the internal pressure. For example, water has an internal pressure of about 1700 atm, while its cohesive energy density is 23 000 atm.

A direct measure of total molecular cohesion per volume of liquid is provided by P_c , since the energy of molecular interactions in the vapor state is negligible. The P_i , on the other hand, measures the infinitesimal cohesive energy change attending infinitesimal volume changes in an isothermal expansion of a liquid. If hydrogen bonding can be considered as forming the basis for three-dimensionally structured complexes, it is not difficult to believe that a very slight expansion of the liquid can be accommodated by small shifts in the directions of hydrogen bonds without breaking the bonds, and therefore that they do not appreciably influence the value of the internal pressure.⁵⁷ Thus the product $P_i V^{2/3}$ may be equated with the dispersion interaction forces for hydrogen-bonded liquids.^{57b} Most of the hydrogen bonds must be broken during the evaporation of the liquid and hence the product $P_c V^{2/3}$ must represent the force necessary both to break the hydrogen bonds and overcome the dispersion-interaction forces.

If the cohesive energy density (P_c) is to be used as a measure of the total molecular-interaction energy contribution to the

pressure, a small correction⁵⁸ of $3RT/2V$ must be added to P_c to give P_c' .

$$P_c' = P_c + (3RT/2V) \quad (12)$$

This correction for the potential energy of a molecule vibrating in a "liquid lattice" about an equilibrium position is determined by the sum of London forces between molecules. The potential energy associated with the external vibrational modes ($\frac{3}{2}RT$) in the liquid state is nonexistent in the gas phase. For many nonassociated liquids, P_c' agrees with P_iV within a few hundred calories per mole.

In the model of the liquid state previously described, it is assumed that the central molecule of a unit cell of liquid is oscillating in a "cage" whose length (from eq 5) is inversely proportional to $PV^{2/3}$. It will also be assumed that the solute molecule dissolved in an associated liquid is not surrounded by a shell of rigid hydrogen bonds, but by a weak, flexible envelope of variable surface area.^{57a} For such a liquid it is reasonable to assume that the effective free volume is not as small as that predicted by considering only the cohesive-energy density. It is proposed that the free volume available to a diffusing molecule in a hydrogen-bonding solvent should be determined from an effective pressure (P_{eff}) derived from the entire interaction energy due to dispersion forces and some fraction n of the hydrogen-bonding energy (eq 13). We now modify eq 8 to use the effective pressure (eq 14).

$$P_{eff} = P_i + n(P_c' - P_i) = nP_c' + (1 - n)P_i \quad (13)$$

$$D = 0.96 \frac{c(RT)^{3/2}}{P_{eff}V^{2/3}M^{1/2}} \quad (14)$$

The enthalpy of activation for viscous flow at constant volume is usually small (of the order of 0.5–0.7 kcal/mol⁵⁹) in keeping with the idea that free volume is a major determinant in viscous flow. However, for hydrogen-bonded liquids the enthalpy of activation for viscous flow at constant volume is a sizable fraction of the enthalpy of activation for viscous flow at constant pressure, suggesting that the breaking of hydrogen bonds is an important factor in these cases. If the enthalpy of activation for viscous flow consists mainly of hydrogen-bonding energy, then a ratio of the activation enthalpy at constant volume to the activation enthalpy $[(\Delta H^*_{vis})_{vol}/(\Delta H^*_{vis})_p]$ equal to unity would imply that a contraction in volume breaks large numbers of hydrogen bonds, offsetting the decrease in fluidity expected from compressing the molecules more closely together. At the other extreme, a value of zero for $(\Delta H^*_{vis})_{vol}/(\Delta H^*_{vis})_p$ for an alcohol would imply that hydrogen bonds are infinitely flexible. In other words, a contraction in volume would, in such a medium, break no hydrogen bonds and the alcohol would behave like a normal liquid. Since the processes of viscous flow and solute diffusion are controlled by the same kinds of forces, we will take the fraction of the total hydrogen-bonding energy appropriately to be included in the description of the effective internal pressure (P_{eff}) in eq 13 to be that given by

$$n = (\Delta H^*_{vis})_{vol}/(\Delta H^*_{vis})_p \quad (15)$$

The parameter n is fairly constant for most alcohols, typically having a value of around 0.68. Thus, to calculate P_{eff} for a typical alcohol 68% of P_c' is added to 32% of P_i (eq 13). This means that the effective free volume available to a molecule in an alcohol solution is a little larger than that predicted from the cohesive energy density, but considerably smaller than that predicted from the internal pressure. For a normal, non-hydrogen-bonding liquid, $P_c' \approx P_i \approx P_{eff}$. For water, $n = 0.90$, implying that the hydrogen-bonding structure of water is not as flexible as is that of alcohols. This may be attributed to the tetrahedral structure produced by hydrogen bonding in water.

In considering the diffusion of a single solute species in dilute solution, it will be assumed that the free volume available to the diffusing molecule will be determined by parameters which are properties of the solvent only. In other words, the value of the quantity $c(P_{eff}V^{2/3})^{-1}$ in eq 14 will be determined by the solvent instead of the solute. A similar treatment has been applied to the theory of solvent effects in infrared spectra.^{60,61} For a series of solvents the best agreement with experimental results in the determination of the fractional decrease of certain vibrational frequencies on solution in a given solvent from the vapor phase of a solute is obtained by calculating the cavity radius of the solute in solution from solvent molecular volume. It seems reasonable that the best correlations of cavity size with solvent volume should be observed for relatively small solute molecules. In the present treatment of diffusion data the diffusion of single species in several solvents is considered and hence contributions to the size of the cavities from the solute should cancel.

The average velocity of a solute (1) relative to molecules of a solvent (2) is given by eq 16, where μ is the reduced mass given by eq 17.

$$v = [8RT/\pi\mu]^{1/2} \quad (16)$$

$$\mu = (m_1m_2)/(m_1 + m_2) \quad (17)$$

Thus for the general case of diffusion in a dilute binary system, eq 14 becomes eq 9. The reduced mass is the only solute-dependent term in the diffusion equation and as long as there are no specific solute-solvent interactions, no other terms should be needed.

Wilke and Chang⁶² expressed data for 155 diffusion-coefficient measurements by an empirical correlation based on the Eyring theory of absolute reaction rates and the Stokes-Einstein equation, with an average deviation of 12% between calculated and observed results. For H₂O and other associated liquids, correlations of diffusion coefficients with solvent parameters were in disagreement with those for unassociated liquids. By assigning a molecular weight to H₂O of 2.6 times the nominal weight, the curve was brought into agreement with the curve for unassociated liquids. The validity of Wilke and Chang's association parameters may be tested with respect to eq 9 using Bonoli and Witherspoon's⁶³ data for diffusion coefficients of paraffin hydrocarbons in water. At 20 °C, $D_{CH_4}/D_{C_2H_6} = 1.24$, which is in excellent agreement with the value of 1.24, also calculated from eq 9 assuming an association parameter of 2.6 for water. A molecular weight of 18 for water yields a value of 1.15 for $D_{CH_4}/D_{C_2H_6}$.

The Lattice Parameter (c). The c factor in eq 10 is related to the packing of molecules in the liquid. If c is fairly constant for most liquids, a plot of D for a particular solute vs. $(P_{eff}V^{2/3}\mu^{1/2})^{-1}$ for a variety of solvents at constant temperature should give a straight line. A plot of the diffusion coefficients for toluene⁶² in a series of straight-chain hydrocarbons, in fact, exhibits a very good correlation ($r = 0.991$). However, when an attempt is made to fit the diffusion coefficient for carbon tetrachloride⁶⁴ in a number of organic solvents of varying properties to the same plot, it is found that the data points for dioxane, CCl₄, cyclohexane, and benzene are all consistently off the line; the points indicating a smaller diffusion coefficient than predicted by $(P_{eff}V^{2/3}\mu^{1/2})^{-1}$. The above four chemically different organic liquids have the common molecular property of being near spherical symmetry.

In their consideration of the viscous flow of liquids, Ewell and Eyring⁴³ found that there was a sharp separation of liquids into two classes; one of which was a class of solvents made up of molecules of spherical symmetry. According to the Eyring theory, the activation energy of viscous flow will be some fraction of the energy of vaporization,

$$(\Delta H^*_{vis})_p = q\Delta E_{vap} \quad (18)$$

Eyring found that for liquids of spherical or approximately spherical fields of force, $q = 1/3$ in eq 18. This is true for CCl_4 , CH_4 , Ar, N_2 , CO, benzene, and cyclohexane. The other 13 liquids studied showed $q = 1/4$. Thus the activation energy for viscous flow for carbon tetrachloride is a factor of $4/3$ times greater than for a liquid of nonspherical symmetry having a similar energy of vaporization. Since the vaporization energy for CCl_4 is about equal to $P_{\text{eff}}V$, it would be reasonable to suppose that multiplying $P_{\text{eff}}V^{2/3}\mu^{1/2}$ times $4/3$ might put the data point for the diffusion coefficient of CCl_4 in dioxane, benzene, cyclohexane, and CCl_4 on the line. This was found to be true.

In view of the diffusion model expressed in eq 10, it is reasonable to suggest that molecules of spherical symmetry are packed in a somewhat different geometrical arrangement than straight-chain hydrocarbons and polar liquids. Thus for these highly symmetrical solvents, the lattice factor (c) is an important correction factor.⁶⁵ For most liquids the lattice factor will be given by

$$c = \frac{1/2 E_{\text{vap}}}{(\Delta H^*_{\text{vis}})_p} \quad (19)$$

and hence for a typical liquid of nonspherical molecules (i.e., $\Delta E_{\text{vap}}/(\Delta H^*_{\text{vis}})_p = 4$), $c = 2$ as derived for a cubic closest packing unit cell.

Water and other associated liquids have much higher viscosities than would be expected from their molecular sizes. The rapid decrease of $(\Delta H^*_{\text{vis}})_p$ as well as the viscosity (η) with an increase in temperature is due to the decrease in the number of hydrogen bonds that have to be broken for viscous flow to take place. For alcohols, in which a rapid equilibrium between short-lived polymeric chains of assorted but finite lengths is occurring, the packing of the molecules in the liquid state is probably close to being entirely controlled by the hydrogen-bonding characteristics of the molecule. It was suggested previously that most of the heat of activation consists of hydrogen-bonding energy and that $(\Delta H^*_{\text{vis}})_{\text{vol}}$ might provide a better description of the diffusion process in associated liquids, since it allows for the slight flexibility of the hydrogen bonds. Furthermore, for the entire composition range of *tert*-butyl alcohol–water mixtures, $(\Delta H^*_{\text{vis}})_{\text{vol}}$, unlike $(\Delta H^*_{\text{vis}})_p$ or η , exhibits a maximum value at 0.90 mol fraction of water characteristic of a structure-sensitive solvent parameter. Thus for associated liquids, the lattice factor may best be described by

$$c = \frac{1/2 E_{\text{vap}}}{(\Delta H^*_{\text{vis}})_{\text{vol}}} \quad (20)$$

Since for a molecule such as a long-chain fatty alcohol the choice between eq 20 (for associated liquids) and eq 19 for unassociated liquids is ambiguous, the use of both eq 19 and eq 20 is unsatisfying. We have therefore modified these equations to give eq 21, a form appropriate for all the liquids studied, by substituting into the denominator a function which approximates $(\Delta H^*_{\text{vis}})_{\text{vol}}$ for alcohols and water and $(\Delta H^*_{\text{vis}})_p$ for nonassociated liquids.

$$c = \frac{1/2 E_{\text{vap}}}{(\Delta H^*_{\text{vis}})_p - 2(1-n)[(\Delta H^*_{\text{vis}})_{\text{vol}} - 700]} \quad (21)$$

In eq 21 n is as defined by eq 15. The constant 700 cal/mol is the average value for $(\Delta H^*_{\text{vis}})_{\text{vol}}$ for nonassociated liquids. Literature values for diffusion coefficients for CCl_4 and toluene show considerably improved correlations (r values of 0.964 and 0.999) in the plots of Figures 14 and 15 (in the microfilm edition) in which the lattice parameter is included than when the correlation is simply against $(P_{\text{eff}}V^{2/3}\mu^{1/2})^{-1}$. While the effect of including this parameter is not a large one, the form of the

dependence of c on solvent is physically plausible and we have included it in eq 10.

Supplementary Material Available. A listing of data from the literature, which were used in calculating quantities needed in the correlations of this paper, together with graphs of other literature data and data from this work, as a function of solvent composition, and the mass spectrometric data of this work (13 pages). Ordering information is given on any current masthead page.

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$$D = \left(\frac{\pi RT}{M} \right)^{1/2} \left(\frac{a}{2} \right) \left[\frac{PV}{RT} - 1 \right]^{-1}$$

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Cyclopropyl Triflates. Neighboring-Group and Solvent Effects

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Abstract: Buffered acetolysis of *exo*-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**) and *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**) suggests an olefin-assisted ionization in the former and competing "normal" and olefin-assisted ionization in the latter. Proposed intermediates are the bicyclo[2.1.1]hex-2-en-5-yl cation (**21**) in the ionization of **8** and the 7-norbornenyl cation (**17**) along with partially opened allylic cation **14** in the acetolysis of **5**. A solvent study indicates very little response to solvent ionizing power in a series of cyclopropyl triflates, which undergo ionization leading to a wide variety of cationic intermediates. Winstein-Grunwald m values lie in the range of typical nucleophilic solvolyses. These results are interpreted in terms of decreased demand for solvent stabilization of trifluoromethanesulfonate anion and a transition state with little charge development.

Cyclopropyl triflates undergo ionization, leading to transition states and intermediates with varying amounts of allylic cationic character.¹ Recently we observed an ionization in which the first cationic intermediate is essentially cyclopropyl in character.² When a neighboring group was appropriately situated, anchimeric assistance to ionization was observed. The key factor which allowed these observations was the fusion of a small ring to the *exo* cyclopropyl triflate, which prevented the allowed electrocyclic ring opening. As part of a study of the requirements for neighboring-group participation to incipient cyclopropyl cations, we have prepared *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**), *exo*-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**), and the cyclopropyl analogue of **8**, *trans*-tricyclo[4.1.1.0^{2,4}]hept-*exo*-3-yl triflate (**10**). It was thought that in these systems, electrocyclic opening during ionization would be sufficiently blocked so as to allow the observation of neighboring-group participation by the appropriately situated group. As part of a general mechanistic investigation, the effect of solvent ionizing power³ (Y) on solvolyzing cyclopropyl triflates was determined. We report here the results of these studies.

Results and Discussion

Preparation of Cyclopropyl Triflates 5, 8, 10, and 11. The desired cyclopropyl triflates were prepared essentially using

procedures developed by Schöllkopf.⁴ Reaction of the olefins 1,3-cyclohexadiene, cyclopentadiene, and bicyclo[3.1.0]hex-2-ene⁵ with dichloromethyl β -chloroethyl ether and methyl-lithium led to the expected β -chloroethyl cyclopropyl ethers **1**, **6**, and **9**, respectively, as a mixture of *exo* and *endo* epimers. Cleavage of **1** with *n*-butyllithium gave an alcohol mixture from which only *exo*-bicyclo[4.1.0]hept-2-en-7-ol (**3**) could be isolated. The *endo*-bicyclo[4.1.0]hept-2-en-7-ol (**2**) underwent facile rearrangement to give a mixture of 2- and 3-cyclohexenecarboxaldehyde (**4**). This facilitated separation of the two isomers and allowed the preparation of pure *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**), uncontaminated with the *endo* epimer.

The addition of β -chloroethoxy carbene to cyclopentadiene gave a mixture of β -chloroethyl cyclopropyl ethers **6** enriched in the *endo* epimer. Cleavage of this mixture with *n*-butyllithium gave an alcohol mixture which was treated directly with a solution of trifluoromethanesulfonic anhydride in pyridine. An exothermic reaction ensued and upon workup, no trace of *endo*-bicyclo[3.1.0]hex-2-en-6-yl triflate could be detected. This is attributed to the probable high reactivity of this *endo*-cyclopropyl triflate, which can undergo concerted ionization and ring opening to a cyclohexadienyl cation, with concomitant release of the strain energy associated with the bicyclo[3.1.0]hex-2-en-6-yl system. This "self destruction"