

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231656413>

Universality in Isomerization Reactions in Polar Solvents

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · JULY 1996

Impact Factor: 2.78 · DOI: 10.1021/jp953502l

CITATIONS

10

READS

13

7 AUTHORS, INCLUDING:



Yavuz Onganer

Ataturk University

66 PUBLICATIONS 1,014 CITATIONS

SEE PROFILE



E. L. Quitevis

Texas Tech University

75 PUBLICATIONS 2,003 CITATIONS

SEE PROFILE

Universality in Isomerization Reactions in Polar Solvents

Mary Vedamuthu,^{†,‡} Surjit Singh,^{†,‡} Yavuz Onganer,^{‡,§} David R. Bessire,[‡] Mary Yin,[‡] Edward L. Quitevis,^{‡,⊥} and G. Wilse Robinson^{*,†,‡,⊥}

SubPicosecond and Quantum Radiation Laboratory and Departments of Chemistry and Physics, Texas Tech University, Lubbock, Texas 79409

Received: November 28, 1995; In Final Form: February 6, 1996[⊗]

Recently it has been shown by Singh and Robinson (SR) that universality and scaling occur in the van der Zwan–Hynes (ZH) model of dipole isomerization reactions near a critical point. This advance in the understanding of chemical reactions was accomplished through the discovery of an analogy of this critical point with the one in the van der Waals equation of state for an imperfect gas. In the present paper, the experimental data of Onganer *et al.* on the cis–trans photoisomerization of merocyanine 540 in *n*-alkyl alcohol and *n*-alkanenitrile solvents, as a function of the solvent shear viscosity and temperature, is analyzed in terms of the ZH model. This model, based on the Grote–Hynes theory, uses a non-Markovian solvent friction characterized by a reactant–solvent coupling strength parameter β , the solvent inertial response time r , and the solvent frictional or viscous response time x . It is found that the photoisomerization data with alcohol solvents fit the ZH model reasonably well, and the fitted parameters β , r , and x are found to lie in the regime near the singularity or the critical point of the ZH model. Utilizing the results of the SR study mentioned above, the experimental isomerization rate is shown to obey a universal scaling relation involving the two scaled variables, $y = (1 - \beta)r$ and $z = (1 - \beta)x^{2/3}$, of the ZH theory in the critical regime. A fractional power law dependence of rate on the inverse of viscosity arises naturally from the theory. The two-variable experimental scaling function is shown to agree with the theoretical scaling function of the ZH model, thus demonstrating the existence of scaling and universality in these experimental data.

1. Introduction

Universality in chemical reactions means the existence of broad features that depend on very few important details of the system under study. The first important law of chemical reactions, the Arrhenius law, is an expression of universality. It states that the main temperature dependence of the rate is through the Boltzmann factor $\exp(-E_0/RT)$, where E_0 is the barrier height, R is the gas constant, and T is the absolute temperature.¹ This factor takes into account the obvious fact that in order for the chemical reaction to take place there must be a certain number of particles in the activated state, which, in turn, is proportional to the Boltzmann factor under the conditions of equilibrium between the reactants and the solvent. This appears to be a contradiction, because if there is an equilibrium, the average velocity of the reactants is zero and the chemical reaction cannot take place. The resolution of this paradox is that the system is really in a state of quasi-equilibrium, which is disturbed in the barrier region to allow a slow passage of reactants to the other side of the barrier to form products. It is well-known that for this assumption to be valid the barrier height should be large, $E_0 \gg RT$. If this assumption is violated, the quasi-equilibrium condition no longer holds and the rate is not proportional to the Boltzmann factor.

One of the first theories to derive the Boltzmann factor using the above quasi-equilibrium idea and to give an analytical expression of the reaction rate was the transition state theory (TST).¹ This theory has been very successful in interpreting chemical reactions in the gas phase. However, its role is very limited in the theory of chemical reactions in solutions. This

is because TST is based on the twin assumptions that the solvent moves sufficiently fast to equilibrate instantaneously and that the reactants proceed to form products directly once they are in the transition state. As shown by Kramers² in his pioneering work on chemical reaction rates more than 50 years ago, both of these assumptions break down when the viscosity η of the solvent is taken into account. His calculations, based on the Langevin and the Fokker–Planck approaches, showed strong dependence on the viscosity as contrasted with the viscosity-independent TST result. The rate is still proportional to the Boltzmann factor, but the prefactor depends on the viscosity of the solvent. In the high-viscosity limit, also called the Smoluchowski limit,³ Kramers found that the prefactor varies as $1/\eta$. This was the second universal feature of chemical reactions to have been discovered.

To describe chemical reactions in solvents, Kramers used the model of a particle crossing a one-dimensional barrier with thermally-assisted activation. His model has been extended and generalized in many directions by using the techniques of nonequilibrium statistical mechanics. For our purposes it is sufficient to describe the seminal work of Grote and Hynes (GH).⁴ They realized that it is insufficient to consider the usual solvent response given by the Langevin equation, where the random force exerted by the solvent on the reactants is assumed to be totally uncorrelated from one time to another. This assumption leads to the usual Stokes law frictional force. Instead, it was shown by GH that one must allow for correlations between the solvent force at different times. This necessitates the use of the generalized Langevin equation that incorporates a finite random force correlation time or memory friction relaxation time. In this equation, the force that the solvent exerts on the reactants (and the products) is given by an integrated response over time. Of course, the Kramers result is obtained from the GH theory formally by letting the random force correlation time go to zero.

[†] SubPicosecond and Quantum Radiation Laboratory.

[‡] Department of Chemistry.

[§] Present address: Department of Chemistry, Atatürk University, Erzurum, Turkey.

[⊥] Department of Physics.

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

TABLE 1: Behavior of the Rate in the ZH Model under Different Damping Conditions and Different Scaling Regimes^a

	underdamped sector, $x \ll r^{3/2}$	critically damped sector, $x \approx r^{3/2}$	overdamped sector, $x \gg r^{3/2}$
weak coupling or nonadiabatic solvation regime, $\beta < 1$	$(1 - \beta)^{1/2}$	$(1 - \beta)^{1/2}$	$(1 - \beta)^{1/2}$
critical coupling, $\beta \approx 1$	$r^{-1/2}$	$0.819r^{-1/2} \approx 0.819x^{-1/3}$	$x^{-1/3}$
strong coupling or polarization caging regime, $\beta > 1$	$r^{-1}(\beta - 1)^{-1/2}$	$r^{-3/2}(\beta - 1)^{-1} \approx x^{-1}(\beta - 1)^{-1}$	$x^{-1}(\beta - 1)^{-1}$

^a Based on ref 16. For explanation of symbols, see text.

2. Power Law Behavior

Many experiments on reactions in solutions have shown deviations from the TST because the reaction rates depend on solvent viscosity. Some of them follow the universal Smoluchowski $1/\eta$ behavior.^{1,5} Recently, however, experimental results that could not be described by either the Smoluchowski or the Kramers formula in a self-consistent manner have begun to appear in the literature.^{5–8} In these experiments the rate is typically described by power laws of the form $(1/\eta)^\alpha$, where the exponent α is a positive fraction less than 1. The derivative of the rate with respect to $1/\eta$ varies as $(1/\eta)^{\alpha-1}$ which goes to infinity as $\eta \rightarrow \infty$. This means that the rate has a singular behavior at the point $1/\eta = 0$, because the rate cannot be expanded in a Taylor series around this point.

Bagchi and Oxtoby,⁹ in a very thorough and involved calculation, showed that the GH theory can be used to explain some of these experimental results. However, they did not explore the implications of the fractional behavior, which clearly implies a singularity in the rate as $\eta \rightarrow \infty$. About the same time as Bagchi and Oxtoby, van der Zwan and Hynes (ZH)^{10,11} created a simple phenomenological model of dipole isomerization reaction rates in polar solvents. In the best tradition of theoretical chemistry, they attempted to capture the most important features of the solvent participation in such reactions, while neglecting irrelevant effects. The inherently complicated many-body problem of reactant–solvent interaction was parametrized by ZH in terms of six quantities, and the rate was obtained using the GH theory.⁴ In the final analysis, the dynamical transmission coefficient κ , which is the ratio of the isomerization rate constant compared with the TST rate constant, depends on just three parameters, which are various combinations of the original six quantities.¹¹ These three parameters are β , the reactant–solvent coupling strength, r , the solvent's inertial response time, and x , the solvent's frictional or viscous response time. On studying their result for the reaction rate for long solvent response times, ZH found that the rate displays a rich variety of behaviors which involve *fractional* and/or negative powers of r and x when the coupling strength parameter β is near 1. Mathematically, this implies that the ZH rate has a singularity in this parameter regime.

3. Critical Reactivity

It is well-known that singularities in physical and chemical quantities occur most commonly in systems undergoing phase transitions. These have been studied for over 100 years in the field of phase transitions and critical phenomena.^{12,13} For example, the difference in the densities of a liquid and coexistent vapor vanishes as a fractional power, called a critical exponent, of the deviation of the temperature from the critical temperature. This exponent equals $1/2$ in the van der Waals theory but is approximately $1/3$ experimentally.¹³ In critical phenomena, a great deal of physical insight into the singularities and a large number of useful mathematical techniques to deal with behavior near them have been developed over the years. Therefore, it seems reasonable that, in order to deal with the singularity in the chemical reaction rate, one should make use of this vast

body of information, which is readily available from textbooks and review articles.^{12–15}

A comprehensive program for this purpose has been undertaken in our laboratory.^{16–18} For details, the original references should be consulted. Here, we summarize the study of the ZH model from the viewpoint of critical phenomena as accomplished by the Singh–Robinson (SR) theory.¹⁶ A critical point occurs in the ZH model at $\beta_c = 1$, $r_c = \infty$, and $x_c = \infty$. Near this point, the rate approaches zero according to various powers (called the critical exponents) of $1/x$, $1/r$, and $|\beta - 1|$. As seen in Table 1, nine exponents are needed to describe the asymptotic behavior of the rate in various regimes. The values of these exponents depend on the coupling strength and the ratio of the inertial and frictional response times of the solvent.¹⁶

Two very important conclusions were reached in the SR theory. The first one has to do with *scaling*, which depends on the fact that near the critical point a suitably scaled rate is a function of suitably scaled solvent response times. Scaling in this problem implies that there are only three independent exponents, and the nine exponents mentioned above are combinations of these three. It was shown in ref 16 (see eq 33) that these are the exponents, $1/2$, 1, and $2/3$, resulting from the scaling of the reaction rate κ , the inertial response time r , and the viscous response time x of the solvent, respectively. If scaling were not valid, there would be no reason to suspect the existence of any relationship between the exponents, and it could well have been thought that all nine exponents mentioned above were actually independent.

The other conclusion of the SR theory involves *universality*, which is the central theme of this paper. In the ZH model, universality implies that the critical exponents depend on very few selected properties of a given system.¹⁴ For instance, the ZH model exponents are found to depend only on the short-time behavior of the memory friction.^{16,17} These exponents do not depend on the actual values of any of the six parameters in this model. For example, if the time dependence of the memory friction is that of a stretched exponential $A \exp(-B|t|^p)$, then the exponent needed for the scaling of the reaction rate is $p/(p + 2)$ and clearly does not involve the values of the parameters A and B . If universality were not valid, the exponents would depend on one or more of these model parameters, in addition to, or instead of, the behavior of the memory friction as a function of time.

Before testing scaling and universality in chemical reactions, we wish to point out the profound consequences that the concept of critical point universality has for the comparison of model systems with experiments. As an example, consider the Ising model originally devised to explain ferromagnetism.¹³ It consists of a three-dimensional lattice that has a spin variable capable of taking only two values attached to each of the lattice points, and it has interactions only between nearest neighbor spin variables. It has been demonstrated experimentally that the Ising model is applicable to uniaxial ferromagnets, uniaxial antiferromagnets, liquids, binary fluid mixtures, and binary alloys.^{12,13} Each of these systems poses an unique many-body problem with all of the usual complications. The mathematics involved clearly makes such systems analytically intractable.

However, a most wonderful conclusion from critical theory is that, near their respective critical points, the critical behavior of all these systems is identical! This sweeping statement is firmly grounded in experiment and is theoretically justifiable through *renormalization group* analysis.^{14,15}

A forerunner of the concept of universality is the so-called law of corresponding states. This law states that if the equations of state of a number of gases are plotted in terms of the reduced variables such as the pressure divided by the critical pressure, etc., all of the data points collapse onto single curves. Typically, the compressibility factor $Z = PV/RT$ is plotted as a function of the reduced pressure for various values of the reduced temperature. The data from many different gases then lie on these "universal" curves. In the same way, in the critical theory, it is expected that the scaled rate will be a universal function of the viscosity-scaled coupling and inertial response-scaled coupling. One very important difference should be noted, however. In the law of corresponding states, the parameters are simply divided by their critical values. In critical theory, the various quantities have to be scaled by suitable critical exponents, which are generally different from unity.

In order to show that universality in chemical reaction theory is valid experimentally, in this paper we deal with the experimental results of Onganer *et al.*⁸ on the photoisomerization of merocyanine (MC) 540 in *n*-alkanenitriles and *n*-alcohols. These authors found that the reaction rates with alkanenitriles as solvents can be fitted to the universal $1/\eta$ law. On the other hand, the experimental reaction rates with alcohol solvents do not follow this law, nor can they be explained consistently by Kramers theory using his intermediate to large friction formula. They did find that the data could be fit to a fractional power of viscosity, which, according to the SR theory, indicates a critical point. According to the SR theory, the critical behavior of all chemical reactions modeled by the ZH theory is identical, irrespective of the values of the quantities such as the moments of inertia of reactants, solvent barrier frequencies, solvent barrier heights, solvent well frequencies, etc.

The implication for the present paper is the following. If the ZH model is applicable to the experimental results of Onganer *et al.*,⁸ and, if the fitted parameters fall in the critical region, then the singular behavior of the photoisomerization rate of MC 540 in all of the solvents is capable of being described by just the three exponents $1/2$, 1 , and $2/3$ of the ZH model. By using suitable scale factors, the single two-variable scaling function $F(y,z)$ defined in eq 34 of ref 16 should describe the reaction rates for all of the solvents!

4. Objectives

According to the preceding, there are two main objectives of this paper. The first one is to determine whether the photoisomerization rate of MC 540 in the alcohol solvents can be described by the ZH model. After a description of the experimental results and analysis of Onganer *et al.*,⁸ a detailed comparison of the experimental data with the ZH model and the parameters of that model can be determined. It develops that the fitting parameters are such that the experimental data are near the critical point of the ZH model.

The second aim of this study is to compare the experimental data with the ZH model in the critical region so as to throw light on the universality in the experimental photoisomerization results. With this in mind, in section 7, a summary of the study of the ZH model near its critical point following SR is presented. In section 8, the parameters obtained in section 6 are combined with the information on the scaling of these parameters to obtain an experimental representation of the scaling function for the

chemical reaction rate. This will be compared with the theoretical scaling function in order to verify the existence of scaling and universality in the experimental data.

5. Experimental Results and Preliminary Analysis

Onganer *et al.*⁸ measured the fluorescence quantum yield of the dye MC 540 in *n*-alkyl alcohol and *n*-alkanenitrile solvents at various temperatures and solvent shear viscosities at atmospheric pressure. By using standard photophysical techniques, they related the quantum yields to the nonradiative rate constant k_{nr} . Normally, this rate constant contains three contributions: internal conversion, intersystem crossing, and photoisomerization. Since the first two processes either do not occur or are negligibly slow, the nonradiative rate constant is essentially equal to k_{iso} , the photoisomerization rate constant.

Employing the standard formula,

$$k_{iso} = A(\eta) \exp(-E_0/RT) \quad (1)$$

where E_0 is the intrinsic (viscosity-independent) barrier height, Onganer *et al.* found that k_{iso} follows this universal Arrhenius behavior. The prefactor $A(\eta)$ is a dynamical quantity that depends on the solvent viscosity η . The intrinsic barrier height E_0 is obtained from isoviscosity plots using a homologous series of solvents. These plots are Arrhenius plots of k_{iso} in these solvents at different temperatures for which the viscosity is a constant. If these isoviscosity lines are essentially parallel, eq 1 is satisfied and the slope of the lines gives the intrinsic barrier height. This slope can be substituted back into eq 1 to obtain $A(\eta)$ as a function of temperature for each solvent. Since the dependence of the shear viscosity on temperature is known, a table of values of $A(\eta)$ as a function of viscosity can be constructed for each solvent.

From the isoviscosity plots, Onganer *et al.* found that the alkanenitrile solvents from acetonitrile to hexanenitrile obeyed eq 1 with an intrinsic barrier height of 2.96 kcal/mol. Similarly, the alcohol data from ethnaol to 1-heptanol obeyed eq 1, yielding a value of 1.39 kcal/mol for the intrinsic barrier height. The values of $A(\eta)$ as a function of η could then be determined for each solvent. They were able to determine, within experimental errors, an approximately solvent-independent intrinsic barrier height, one for alcohols and one for nitriles. This indicates that the solvent-polarity effects can be neglected in this analysis.

How does $A(\eta)$ in these experiments depend on viscosity? In ref 8, Kramers theory for the intermediate to large friction regime was used to try to understand the behavior of $A(\eta)$ by assuming that the frictional parameter ζ occurring in that theory is proportional to η . It was found that for alkanenitriles, $A(\eta)$ could be fit well to the Smoluchowski universal limit of the Kramers theory, $A(\eta) \propto 1/\eta$. On the other hand, the data on the alcohols could not be explained by the Kramers formula without contradictions. However, the reaction rate in alcohols could be represented approximately by an equation of the form $A(\eta) \propto 1/\eta^{0.6}$.

Such fractional exponents cannot arise in the Kramers theory. However, they are found abundantly in models based on the GH theory.^{10,11,16-18} For example, as mentioned above, they occur in the ZH model, the rate behavior in this model showing a multitude of exponents near a critical reactant-solvent coupling and large viscosity.^{10,11,16}

With this in view, in the next section we study the data on alcohols using the ZH model of isomerization in dipolar solvents.

6. Data Analysis Using the ZH Model

For details of the ZH model, original work should be consulted.^{10,11} For a brief summary, see section II of SR.¹⁶ The

TABLE 2: Parameters Resulting from the Fitting of the Experimental Reduced Rate to the Theoretical Reduced Rate^a

alcohol	C' (ps)	C'' (cP ⁻¹)	β	r	y	x (lowest)
ethanol	1.65×10^{-3}	2.89×10^6	1.01	2.22×10^4	-222	1.68×10^6
1-propanol	1.38×10^{-3}	2.34×10^6	1.01	3.58×10^4	-358	2.13×10^6
1-butanol	1.39×10^{-3}	2.31×10^6	1.01	7.82×10^4	-782	2.61×10^6
1-pentanol	1.13×10^{-3}	1.28×10^6	1.015	1.75×10^5	-2625	1.74×10^6
1-hexanol	0.98×10^{-3}	0.97×10^6	1.02	1.81×10^5	-3620	1.80×10^6
1-heptanol	1.07×10^{-3}	1.03×10^6	1.02	2.51×10^5	-5020	2.19×10^6

^a For definitions of symbols, see text.

reduced rate κ , which is defined as the isomerization rate divided by the TST rate, is given by the real positive solution of the equation¹¹

$$\kappa = \left(\kappa + \frac{\beta(x + \kappa r^2)}{1 + \kappa x + \kappa^2 r^2} \right)^{-1} \quad (2)$$

where the various symbols are explained below. There is assumed to be a coupling between the reactant and the solvent dipoles which arises in the following way. If the reactant dipoles change their relative angular orientations, the solvent dipoles experience different electrical torques because of the usual dipole-dipole interactions between the two kinds of dipoles. How strong is this effect, and how fast does it take place? The parameter β is a measure of the strength of this effect, and the other two parameters r and x measure the rate of response of the solvent to this interaction. Two parameters are required here because the response can be caused by inertial, *i.e.*, nonfrictional effects, represented by r , or frictional effects, represented by x . It should be noted here that ZH neglected frictional effects in their first paper¹⁰ but in their next paper¹¹ these were taken into account. The SR theory is based on ref 11.

In order to use eq 2 for understanding the experimental results, we introduce two linear relations, one between the experimental and the theoretical reduced rates and the other between the experimentally determined viscosity and the theoretical frictional parameter,

$$\kappa = C'A(\eta), \quad x = C''\eta \quad (3)$$

where C' and C'' are suitable scale factors.

By using the experimental values⁸ of $A(\eta)$ versus η for each alcohol, as described in the previous section, and fitting these to the theoretical rate from eq 2, along with eqs 3, the various parameters can be determined. Standard nonlinear least squares fitting routines were used. The resulting parameters are listed in Table 2. Also included are the lowest values of the frictional parameter x (corresponding to the smallest viscosity) of the ZH theory for each alcohol. The error-bar deviations between the experimental and theoretical rates are at most 9%.

The parameter C' is about 10^{-15} s, which implies an attempt frequency of about 10^{15} /s. It is difficult to give a more physical meaning to this parameter at this stage of the theory, as this necessitates a thorough many-body analysis of the isomerization problem, which is clearly beyond the scope of this paper. Fortunately, as far as the critical analysis is concerned, the exact value of the C' parameter is unimportant. The largeness of the parameter C'' , as seen in Table 2, causes the value of the frictional response time x to be very large. From the fifth column of Table 2, one can see that the inertial response time parameter r is also very large. Finally the solvent-solute coupling strength parameter β is close to unity, as seen in column 4 of this table.

Some years ago, Sivakumar *et al.*⁷ used the ZH model, among other models, to analyze their data on the photoisomerization of 4,4'-dimethoxystilbene and *t*-stilbene in *n*-alkanenitriles. On fitting their data to a power-law form $A(\eta) \propto \eta^{-\alpha}$, they found that $\alpha = 0.51$ for *t*-stilbene and $\alpha = 0.44$ for 4,4'-dimethoxystilbene. Clearly their data also lie in the neighborhood of the critical point. They compared their results with the ZH theory, but their method of data analysis was different from ours in two respects. They assumed that the prefactor $A(\eta)$ in eq 1 is exactly equal to the ZH reactive frequency $\kappa\omega_{b,eq}$, where $\omega_{b,eq}$ is the frequency corresponding to the equilibrium solvated barrier. In our notation this implies that the scale factor C' is assumed to be the same for all solvents. Also, they utilized only the overdamped sector ($x \gg r^{3/2}$) of the ZH theory. Nonetheless, values of β obtained in their analysis ranged from 0.950 to 1.011, a clear indication that the data, just as the data of Onganer *et al.*,⁸ fall near the critical point of the ZH theory. It will be very profitable to reanalyze the data of Sivakumar *et al.*⁷ using the SR theory, which was not available when their work was published.

Summarizing our analysis of the data of ref 8, the ZH model is found to be applicable to the isomerization rates of MC 540 in alcohols, and the fitted parameters are such that $x \gg 1$ and $r \gg 1$, with β close to 1. Also the expected errors in x , r , and β are found to be 2, 20, and 0.5%, respectively. In general, how high should x and r be and how close should β be to 1? The answer depends on the system under consideration, but a rule of thumb is that the values of the parameters x and r should be greater than a few hundred and the relative distance of β from its critical value should not be more than a few percent. In our case, the conditions are clearly met even when the error bars mentioned above are taken into account. Therefore, in the next section we present the results of a study of this model near its critical point.

7. ZH model in the Critical Regime

A detailed study of the ZH model near its critical point was presented in ref 16. In this section we summarize these results with an emphasis on the mathematical analogy between critical phenomena for liquid/gas phase transitions and those of the ZH model. To begin with, we assume that the frictional response time x is much larger than the inertial response time r . This case has been called the *overdamped solvent regime* by ZH. Therefore, r can be neglected in eq 2 to obtain,¹¹

$$\kappa = \left(\kappa + \frac{\beta x}{1 + \kappa x} \right)^{-1} \quad (4)$$

or, on rearranging,

$$\kappa^3 x + \kappa^2 + \kappa x(\beta - 1) - 1 = 0 \quad (5)$$

This is a cubic equation, like the van der Waals equation in the theory of fluids.^{12,13} Proceeding exactly as in the van der Waals theory, it can be shown that eq 5 has a critical point at $\beta_c = 1$,

$\kappa_c = 0$, and $x_c = \infty$. Physically, this implies that, for large solvent frictional response times ($x_c = \infty$), the isomerization rate is very small ($\kappa_c = 0$) near a critical coupling strength ($\beta_c = 1$) and its behavior changes dramatically near this critical point. This is completely analogous to the behavior of a van der Waals fluid near its critical point. Of course, it should be kept in mind that there are no thermodynamic phases in the κ - β - x space of the chemical reaction theory. Thus, the analogy is at a mathematical level only. However, the analogy is powerful and leads to the introduction of new physical ideas like scaling and universality in the theory of chemical reactions.

We will now explain this analogy more fully by using the results for this overdamped case. The results for the ZH model for this case are presented in the fourth column of Table 1. For $\beta < \beta_c (\equiv 1)$ and $x \rightarrow \infty$ one finds that¹¹

$$\kappa \approx (1 - \beta)^{1/2} \quad (6)$$

This is the *nonadiabatic solvation regime* of ZH: the coupling is weak, and the response of the solvent is slow. Nonetheless, the reaction does take place at a very slow rate, approaching zero as the square root of the "distance" from critical coupling. This is precisely the behavior of the van der Waals gas on the coexistence curve below and near the critical temperature,^{12,13}

$$\frac{V_{\text{gas}} - V_c}{V_c} \approx 2 \left(1 - \frac{T}{T_c} \right)^{1/2} \quad (7)$$

Clearly, except for numerical factors, the analogy is

$$\frac{V_{\text{gas}} - V_c}{V_c} \leftrightarrow \kappa, \quad T \leftrightarrow \beta \quad (8)$$

Exactly at critical coupling, eq 4 yields¹¹

$$\kappa \approx x^{-1/3} \quad (9)$$

which indicates that the rate goes to zero with a fractional power of the frictional response rate. The corresponding equation in the van der Waals theory is the behavior at the critical isotherm^{12,13}

$$\frac{V_{\text{gas}} - V_c}{V_c} \approx -(2/3)^{1/3} \left(\frac{P - P_c}{P_c} \right)^{1/3} \quad (10)$$

which gives the final piece of the analogy:

$$\frac{P - P_c}{P_c} \leftrightarrow x^{-1} \quad (11)$$

In the strong coupling regime, called the *polarization caging regime*,^{1,8} one has¹¹

$$\kappa \approx x^{-1} (\beta - 1)^{-1} \quad (12)$$

In the van der Waals theory, the corresponding equation is^{12,13}

$$\frac{V_{\text{gas}} - V_c}{V_c} \approx (2/3) - (1/6) \left(\frac{P - P_c}{P_c} \right) \left(\frac{T - T_c}{T_c} \right)^{-1} \quad (13)$$

a relation which is usually expressed in terms of the bulk modulus or the compressibility.

In ref 16, this analogy with critical phenomena was fully exploited, and, by using standard critical theory methods,^{12,13} it was shown that the chemical reaction rate for general damping obeys a scaling relation given by

$$\kappa r^{1/2} = F(y, z), \quad y = (1 - \beta)r, \quad z = (1 - \beta)x^{2/3} \quad (14)$$

where the scaling function $F(y, z)$ is the real positive solution of the equation,^{16,19}

$$F^2 - y - F^{-2} \left(1 + \frac{|z|^{3/2}}{F|y|^{3/2}} \right)^{-1} = 0 \quad (15)$$

The scaling relations 14 express the fact that, near the critical point, the rate κ scaled by $1/r^{1/2}$ (that is, multiplied by $r^{1/2}$) is a function of $1 - \beta$ scaled by $1/r$ and $1/x^{2/3}$. These quantities then represent two scaled critical "distances". These particular combinations are dictated by the form of the memory friction kernel chosen by ZH.^{16,17} It should be remembered that away from the critical point, for example at $\beta = 5$, the rate cannot be written in the scaling form and depends on all three parameters β , r , and x independently.

The quartic eq 15 for the scaling function F can be solved by standard methods for given values of y and z . However, it is more illuminating to obtain its asymptotic behavior in various regions near the critical point. This behavior can be substituted in eqs 14 to yield the rate in the corresponding regions. These results have already been displayed in the three data columns of Table 1. It is seen that the rate is described by various powers of $|1 - \beta|$, x , and r . These powers, called the critical exponents, arise in special circumstances described in the table. In the general case, the rate has to be obtained using eqs 14 and 15. A discussion of these results and a pictorial representation of scaling can be found in ref 16.

8. Comparison of the Experimental Results with the Critical Theory

From Table 2 it is clear that the values of various parameters are such that the experimental results on alcohols are in the critical region: $\beta \approx 1$; and x and $r \gg 1$. Since, as seen in Table 2, the reactant-solvent coupling strength parameter β is greater than 1, the strong-coupling or polarization caging regime is involved.^{7,11} This implies that the bottom row in Table 1 should apply. A natural question is which *column* of Table 1 should be used? The results in the three data columns become applicable depending on the relative values of x and $r^{3/2}$. From Table 2 it is found that the lowest value of x listed there is 1.68×10^6 and the highest value of r is 2.51×10^5 , so that the lowest value of the ratio $x/r^{3/2}$ is about 10^{-2} . Therefore, as seen in the last row and first data column of Table 1, for this low value of x the rate is independent of x , and thus independent of viscosity (recall from eq 3 that $x \propto \eta$). In the last two columns of Table 1 we see the effects of increasing viscosity, or increasing x . The rate then becomes proportional to $1/x$ ($= 1/C'\eta$). The experimental rate for the alcohols was found to be neither independent of η nor proportional to $1/\eta$. Therefore the experimental results lie somewhere in the region between either the first and second or the first and third data columns in the bottom row of Table 1.

According to the above discussion, the experimental rate data should not fit a single power law. However, let us suppose that critical ZH theory¹⁶ is not used, and one simply tries to "fit" the data on the alcohols to a single "power law".⁵⁻⁸ Keeping in mind the discussion in the previous paragraph, it is clear that the data may very well appear to "fit" an exponent that lies between 0 (viscosity-independent behavior) and 1 (Smoluchowski behavior). This is precisely what was found by Onganer *et al.*⁸ Since the critical study of the ZH theory was published only recently,¹⁶ and was then unavailable, they tried to fit all of the data points for alcohols to a single exponent,

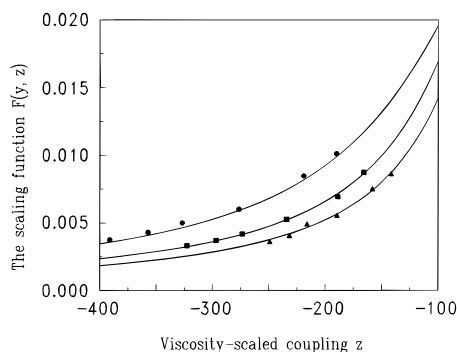


Figure 1. Plot of the scaling function $F(y, z)$ versus viscosity-scaled coupling z for various values of the solvents' scaled inertial response times y . The solid curves are the theoretical scaling function calculated from eq 15. The experimental scaling function points are as follows: triangles, ethanol, $y = -222$; squares, 1-propanol, $y = -358$; circles, 1-butanol, $y = -782$.

obtaining a value of 0.6 which is between 0 and 1, as might be expected. A similar argument can be made for the fractional exponents found in the study of Sivakumar *et al.*⁷

Now that the critical study of the ZH model is available, a more thorough analysis can be performed. One can try to see if the experimental data obey the scaling relation given in eq 14 and, if so, calculate the experimental scaling function and compare it with the theoretical scaling function given in eq 15. This is done as follows. The data for one alcohol, such as ethanol, are taken. The values of $A(\eta)$ for various values of η and the various fitting parameters are available.⁸ From the unique values of r and β listed in Table 2, first y is calculated by using eq 14. Next, for each temperature dependent value of η for ethanol, the corresponding value of x is calculated by using eq 3 and C'' from Table 2. Then, eq 14 is used to calculate z , and eqs 3 and 14 are used to obtain the corresponding values of the experimental scaling function. This is repeated for each value of viscosity for this alcohol, and the resulting data points can be plotted as the experimental scaling function. The ethanol points obtained in this way are shown as triangles in Figure 1. The theoretical scaling function can be obtained by solving eq 15 numerically for the specific value of y ($y = -222$ for ethanol) and for the applicable range of z values. This is shown as the lower curve in Figure 1, which is seen to coincide well with the six experimental points for ethanol.

The same exercise is repeated for the remaining five alcohols, each corresponding to a unique value of y given in Table 2 and the appropriate range of z values. All the theoretical curves are obtained using the single scaling function given by eq 15. For clarity, the results for the three lower alcohols are depicted in Figure 1, while those for the remaining three are shown in Figure 2. The agreement between the experimental points obtained from the isomerization data for various alcohols at different temperatures and the theoretical function is quite reasonable for all of the alcohols, though better fits were obtained for the lower alcohols than for the higher ones. Since the maximum difference between the scaling functions from theory and experiment is the about the same as the difference between the experimental and the fitted rates in section 6, it is likely that the deviations are caused by a larger experimental uncertainty for the more viscous higher alcohols.

9. Summary and Discussion of Results

We began this work by fitting the experimental photoisomerization data in alcohol solvents to the ZH theory. We found that the data fit the ZH theory quite well. If the data had not fit the ZH theory, one would have to look for another model,

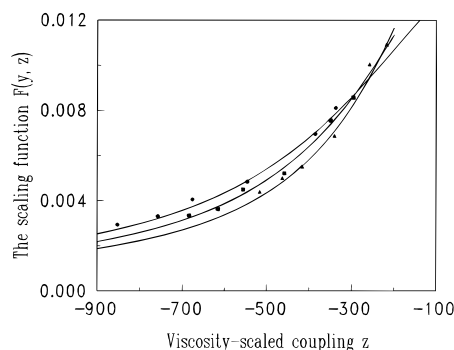


Figure 2. Same as Figure 1. The experimental scaling function points are as follows: triangles, 1-pentanol, $y = -2625$; squares, 1-hexanol, $y = -3620$; circles 1-heptanol, $y = -5020$.

such as the Bagchi–Oxtoby model.⁹ On realizing that all of the data in the alcohol solvents not only fit the ZH theory, but the parameters fall into the critical region of the model, we plotted the 36 experimental scaling function points, as calculated here, together with the single scaling function expression given by eq 15. The fact that all alcohols have the same scaling function is an indication of critical point *universality*. It bears repeating that only a “single” scaling function given by eq 15 was required to fit the data over the whole parameter range. The fact that the rate had to be scaled by the powers given in eq 14 provides support for the concept of scaling and the particular memory friction kernel used in the ZH model.

We now discuss the figures. The negative values of y and z , for values of β greater than unity, simply mean that the data are in the polarization caging regime (bottom row of Table 1) for all of the alcohols studied. Numerically large values of z imply large x and, therefore, large viscosity, causing both the rate and the scaling function to decrease as the viscosity increases. Different alcohols correspond to different values of y because the inertial response time r on which y depends must certainly be different for each alcohol.

What kind of plots would have resulted if scaling and/or universality were not valid? Had the parameters of the ZH model not been near the critical point, the experimental points would have been scattered all over the plots and would not have been near the theoretical scaling function curves. This serves to remind us that the concept of scaling is valid only near the critical point. Even if scaling were valid, critical point universality could have failed in the following way. The experimental points would appear to lie on curves essentially similar in shape to the theoretical ones, but there would be no way to make them coincide by sliding the curves in the horizontal or vertical directions. This would have meant that it is impossible to find suitable values of the scale factors C' and C'' . The fact that everything has fallen into place in our calculation is a very clear signal that the experimental data on the photoisomerization of MC 540 in alcohol solvents all lie in the neighborhood of the critical point, and, furthermore, that the data can be described by a single scaling universal function describing the critical phenomena in the ZH model.

Finally, let us comment on the experimental data on the alkanenitriles. Onganer *et al.*⁸ found that these data could be represented by the $1/\eta$ law of Smoluchowski. Looking at Table 1, it is found that this behavior occurs in the bottom row (strong coupling region) and second (critical damping sector) and third (overdamped sector) data columns. In order to show that the scaling function given by eq 15 is applicable to the alkanenitriles, we must show that the $1/\eta$ behavior follows from the scaling function. As an example, we discuss the overdamped sector of the third column, where the critical damping of the

second column can be dealt with in a similar way. In the overdamped ($x \gg r^{3/2}$) sector, both y and z approach $-\infty$ with $|z| \gg |y|$ and the scaling function given by eq 15 goes to zero as

$$F(y,z) \approx |y|^{1/2}/|z|^{3/2}, \quad y \rightarrow -\infty, z \rightarrow -\infty \quad (16)$$

Thus, the rate goes to zero as

$$\kappa \approx \frac{1}{(\beta-1)x} \quad \beta > 1, x \rightarrow \infty, r \rightarrow \infty, x \gg r^{3/2} \quad (17)$$

Rewriting this equation in terms of the reduced rate from eq 3, it is found that

$$A(\eta) = B/\eta \quad (18)$$

where B is given by the combination

$$B = 1/C'C''(\beta-1) \quad (19)$$

Reported by Onganer *et al.*⁸ was an unique positive value of B ($A_1A_2/2$ in their notation), which is completely consistent with the fact that $\beta > 1$, as required for the validity of eqs 16–19. Unfortunately, until more data are available on the alkanenitriles in the low damping sector (lower viscosities), it is not possible to obtain values of the individual parameters in eq 19. Therefore it is not possible to calculate the scaling function uniquely for these solvents. However, we have clearly shown that the Smoluchowski behavior of the rate in the alkanenitrile solvents is completely consistent with and follows from the same scaling function as the one used for the alcohol solvents, eq 15.

10. Concluding Remarks

It is quite remarkable that the data on the photoisomerization rate of MC 540 in both alkanenitriles and alkyl alcohols can be explained by the critical properties of the simple but powerful ZH model based on the GH theory. By hindsight, the fact that the data all lie in the high-viscosity region of various solvents is perhaps not too surprising because it is so difficult to “eliminate” this experimental property. In fact, many groups have tried very hard to lower the solvent viscosity so as to see the so-called Kramers turnover experimentally.¹ On the other hand, the circumstance that the reactant–solvent coupling parameter is so close to its critical value of unity is a lucky stroke, since it has made possible the demonstration that photoisomerization rates of MC 540 in different polar solvents obey scaling and universality.

A comment is in order here about the values of the fitted parameters obtained by us. As mentioned above, the values of the exponents follow from the SR study. How does one understand the fitted values of C' and C'' on one hand and those of β , r , and x on the other? Our main purpose was to show the existence of scaling and critical point universality in the experiments on photoisomerization in polar solvents. The whole idea of the universality concept is that this demonstration does not, in fact must not, depend on the actual values of the various scale factors. A more microscopic study of the chemical reaction would have to be undertaken in order to “explain” the values of the scale factors.

The critical point universality found here is not restricted to the particular reactions and solvents studied in this paper. Surely, the data of Sivakumar *et al.*,⁸ being near the critical point of the ZH theory, will also obey universality. As far as other types of chemical reactions are concerned, using one's experience from the theory of critical phenomena, it can be said that this new universality will be seen in any chemical reaction

in which there is a singularity in the rate, *i.e.*, where the rate depends on viscosity through critical exponents that are not positive integers. In fact, it is possible that there are only a few values of the basic exponents that occur in the majority of chemical reactions.

For example, considering the important work of Bagchi and Oxtoby,⁹ there is no doubt that this model too has a critical point, because, in comparing their model with experiment, Bagchi and Oxtoby did obtain fractional exponents, which is one of the key features of any critical theory. Both the ZH and the Bagchi–Oxtoby model are based on the purely parabolic GH theory. It will certainly be interesting to see if one needs improved theories with a finite well, which go beyond the GH theory, in order to explain certain other experiments.^{17,18} Clearly, one needs to do experiments in systems in which the well is not too deep.

Acknowledgment. Financial support at SPQR laboratory was provided by the Robert A. Welch Foundation (Grants D-0005 and D-1094), by private donations from one of the authors (G.W.R.) and the G. Wilse Robinson, Jr., Trust, Kansas City, MO. E.L.Q. acknowledges the support of the Robert A. Welch Foundation (Grant D-1019).

References and Notes

- (1) Hynes, J. T. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 4, p 171.
- (2) Kramers, H. A. *Physica (Utrecht)* **1940**, 7, 284.
- (3) Smoluchowski, M. V. *Ann. Phys. (Leipzig)* **1915**, 48, 1103.
- (4) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, 73, 2715.
- (5) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: Oxford, UK, 1986. Waldeck, D. H. *Chem. Rev.* **1991**, 91, 415.
- (6) Keery, K. M.; Fleming, G. R. *Chem. Phys. Lett.* **1982**, 93, 322. Vesko, S. P.; Fleming, G. R. *Chem. Phys.* **1982**, 65, 59. Vesko, S. P.; Waldeck, D. H.; Fleming, G. R. *J. Chem. Phys.* **1983**, 78, 249. Courtney, S. H.; Fleming, G. R. *Chem. Phys. Lett.* **1984**, 103, 443. Courtney, S. H.; Fleming, G. R. *J. Phys.* **1985**, 83, 215. Kim, S. K.; Fleming, G. R. *J. Phys. Chem.* **1988**, 92, 2168.
- (7) Sivakumar, N.; Hoburg, E. A.; Waldeck, D. H. *J. Chem. Phys.* **1989**, 90, 2305.
- (8) Onganer, Y.; Yin, M.; Bessire, D. R.; Quitevis, E. L. *J. Phys. Chem.* **1993**, 97, 2344.
- (9) Bagchi, B.; Oxtoby, D. *J. Chem. Phys.* **1983**, 78, 2735.
- (10) van der Zwan, G.; Hynes, J. T. *J. Chem. Phys.* **1983**, 78, 4174.
- (11) van der Zwan, G.; Hynes, J. T. *Chem. Phys.* **1984**, 90, 21.
- (12) Fisher, M. E. *Rep. Prog. Phys.* **1967**, 30, 615.
- (13) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: Oxford, UK, 1971.
- (14) Fisher, M. E. In *Critical Phenomena*; Hahne, F. J. W., Ed.; Lecture Notes in Physics; Springer: Berlin, 1983; Vol. 186, pp 1–139.
- (15) *Phase Transitions and Critical Phenomena*; Domb, C., Green, M. S., Eds.; Academic: New York, 1971–1983. *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic: New York, 1983–1992.
- (16) Singh, S.; Robinson, G. W. *J. Chem. Phys.* **1994**, 100, 6640.
- (17) Singh, S.; Krishnan, R.; Robinson, G. W. *Phys. Rev. Lett.* **1992**, 68, 2608. Singh, S.; Krishnan, R.; Robinson, G. W. *Phys. Rev. E* **1994**, 49, 2540. Singh, S.; Robinson, G. W. *J. Chem. Phys.* **1995**, 103, 4920.
- (18) Singh, S.; Robinson, G. W. *Chem. Phys.* **1994**, 183, 365. Singh, S.; Robinson, G. W. *J. Phys. Chem.* **1994**, 98, 7300. Singh, S.; Robinson, G. W. *J. Phys. Chem.* **1994**, 99, 2764. Singh, S.; Robinson, G. W. *Chem. Phys.* **1995**, 198, 257.
- (19) The scaling function expression quoted in eq 34 of ref 16 is valid only for $y > 0$ and $z > 0$. Equation 14 of the present paper is a generalization for all real values of y and z .