Reaction Kinetics and Critical Phenomena: Rates of Some First Order Gas Evolution Reactions in Binary Solvents with a Consolute Point

Yeong Woo Kim and James K. Baird*

Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35899

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We have measured the rate of carbon dioxide evolution in the aniline catalyzed decomposition of acetone dicarboxylic acid in a mixture of isobutyric acid + water near its consolute point. Within a temperature interval of 1 °C, which included the critical solution temperature, the first-order rate constant oscillated in magnitude by about 10% as it passed through three complete cycles of slowing down followed by speeding up. Whereas we can find no ready explanation for the speeding up, we suggest that, because the mixture contained no inert components, the slowing down should belong to the Griffiths−Wheeler class of strong critical effects [*Phys. Rev. A* **1970**, *2*, 1047]. As a check on this conclusion, we have measured the rate of the S_N1 decomposition of benzene diazonium tetrafluoroborate in 2-butoxyethanol + water near the lower critical solution temperature and also the rate of the acid-catalyzed decomposition of ethyl diazoacetate in isobutyric acid + water near the upper critical solution temperature. Both of these reactions evolve nitrogen. In the first reaction, 2-butoxyethanol is inert, whereas in the second, isobutyric acid is inert. In both cases, because there was one inert component, we regarded the response of the rate constant to temperature in the critical region to be representative of the Griffiths−Wheeler class of weak critical effects. Within our accuracy of measurement of about 2% in the rate constant and about 1 mK in the temperature, we could detect no effect of the critical point on the rates of either of these reactions, suggesting that a *weak* effect may be too small to be seen with our experimental apparatus. The successful observation of a critical effect in the rate of decomposition of acetone dicarboxylic acid proves, however, that kinetic critical phenomena are observable in heterogeneous reactions.

1. Introduction

The consolute point is an extremum in the temperature vs mole fraction phase diagram of a constant pressure binary liquid mixture where the homogeneous solution first begins to separate into two immiscible layers. The extreme value of the temperature along the boundary separating the two immiscible liquids is called the critical solution temperature, T_c^0 A binary mixture having a liquid−liquid-phase boundary that is *concave down* has an upper critical solution temperature (UCST) and exists as one phase above the boundary and as two phases below it.[1] By contrast, a binary mixture having a liquid−liquid-phase boundary that is *concave up* has a lower critical solution temperature (LCST) and exists as two phases above the boundary and as a single phase below it.[1] Upon introduction of a reactant or a catalyst to the liquid, a chemical reaction can often be initiated. This permits these mixtures to be used to study the effect of the critical temperature on the net rate of reaction.[2−8]

The principle of universality predicts that sufficiently close to the critical point the various thermodynamic properties of liquids and liquid mixtures are governed by universal functions of the difference between the temperature and the critical temperature.[9−14] The search for critical effects in chemical reaction rates near a consolute point serves as a test of the applicability of the principle of universality to reaction kinetics. In pursuit of kinetic critical phenomena, we have measured the rates of five different S_N1 hydrolysis reactions near the equilibrium consolute points of three water-based binary liquid mixtures.[4,5] In each case, we observed slowing down of the net rate of reaction as the temperature approached the critical temperature.

To understand the role played by the presence of coexisting phases on the kinetics, we have recently reinvestigated the rates of two of these reactions, namely, 2-chloro-2-methylbutane in isobutyric acid + water (UCST)[6,7] and 2-bromo-2-methylpropane in triethylamine + water (LCST).[7] Using an improved conductance meter to follow the extent of the reaction and strong stirring in order to keep any coexisting phases well mixed, we observed slowing down in both cases at temperatures above critical and speeding up at temperatures below critical.[7] Because there is just one phase above the critical temperature in the first reaction and two phases above the critical temperature in the second, the results of these two experiments combine to suggest that the observed reaction rate effects are associated with the critical point and are not just a simple artifact of the coexistence of two phases.

In addition to these first-order reactions, we have searched for critical slowing down in the rate of the sodium hydroxide catalyzed saponification of ethyl acetate in 2-butoxyethanol + water (LCST), where the rate controlling step is bimolecular and the kinetics are second-order.[8] We followed the time course of the extent of reaction by measuring the conductivity. In contrast to the S_N1 reactions,[6,7] we observed in this bimolecular reaction a slowing down effect that was confined to the one phase region below the critical solution temperature.[8]

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* To whom correspondence should be addressed.

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In the hopes of expanding upon these early results, we have posed the following question: Can a critical reaction rate effect be detected by following the extent of reaction using a method other than the measurement of the conductivity of the liquid phase? For example, is it possible to observe a critical effect in a heterogeneous reaction where the progress of the reaction is followed by measuring the rate of appearance of a phase that is not completely miscible with the original binary liquid mixture? In an attempt to answer this question, we report herein the results of the study of three gas forming reactions, where the kinetics can be determined by following the rate of evolution of the gas. The first of these is the aniline catalyzed decarboxylation of acetone dicarboxylic acid in isobutyric acid + water (UCST). The products are acetone and carbon dioxide, and the rate law is first order in the concentration of acetone dicarboxylic acid.[15] The second reaction is the decomposition of benzenediazonium tetrafluoroborate in 2-butoxyethanol + water (LCST). The products are phenol, fluoroboric acid, and nitrogen. The rate law is first order in the concentration of benzenediazonium tetrafluoroborate.[16,17] The third reaction is the acid-catalyzed decomposition of ethyldiazoacetate in isobutyric acid + water (LCST). The products are ethyl hydroxyacetate and nitrogen. The rate law is first order in the concentration ethyldiazoacetate[18] and first order in the concentration of H^+.[19] Use of a pH meter shows that isobutyric acid + water at its consolute composition has pH = 2. Because the acidity is high while the concentration of ethyldiazoacetate is low, the observed rate is pseudo-first-order overall.

To establish the theoretical context for our experiments, we introduce in section II the concept of the extent of reaction and describe how it connects the kinetics to the thermodynamics in a critical mixture. In section III, we describe the details of our experiment. In section IV, we analyze our results in terms of the principle of critical point universality and draw our conclusions. In the Appendix, we provide an explanation of our method of measuring the rate of gas evolution using a gas dilatometer.

II. Theory

(1) Extent of Reaction. The extent of reaction can be defined by considering a reversible elementary reaction written in the form

$$\nu_1(1) + \nu_2(2) \rightarrow \nu_3(3) + \nu_4(4) \qquad (1)$$

In this equation, reactants (1) and (2) are converted into products (3) and (4). The respective stoichiometric coefficients are ν_1, ν_2, ν_3, and ν_4. If we let $c_i(0)$ be the initial concentration of species, (i), then the concentration, c_i, at a later time, t, is $c_i = c_i(0) \pm \nu_i\xi$ where ξ is the extent of reaction, and the upper sign applies to products while the lower sign applies to reactants. The initial value of ξ is zero, and its equilibrium value at the end of the reaction is ξ_e. The net rate of reaction is the time derivative, $d\xi/dt$.

(2) Effects Linked to the Extent of Reaction. In our experiments to this point,[4−8] we have encountered several effects that serve to link the critical point with the extent of reaction. Two of these play a role in the case of a gas evolution reaction.

First, the dissolution of reactants and reaction products in a binary mixture usually causes a noticeable shift in the critical temperature. As a consequence, it becomes necessary to draw a distinction between the critical solution temperature, T_c^0, of the solvent mixture and the critical solution temperature, T_c, of the multicomponent mixture which includes the products and reactants at chemical equilibrium. We have observed experimentally that

$$T_c = T_c^0 + ac \qquad (2)$$

where a is an empirical coefficient, which has a different value for each mixture, and c is the initial molar concentration of the added reactant.[6,7] In actuality, the value of T_c is determined by the value of ξ_e; nevertheless, T_c can be connected to c, because of the stoichiometric relation that exists between the reactant and the products and also because all of the reactions that we have carried out so far go essentially to completion. If at chemical equilibrium the actions of the catalyst, the reaction products, and any remaining reactant combine to enhance the mutual solubility of the original solvent pair, an UCST is lowered ($a < 0$), whereas an LCST is raised ($a > 0$).[1,20−22] On the other hand, when the presence of these components inhibits the mutual solubility of the original pair, an UCST is raised and an LCST is lowered.[1,20−22]

Second, when the thermostat temperature, T happens to lie between T_c^0 and T_c, a liquid−liquid-phase transition will occur in the mixture during the course of the reaction.[6,7] The elapsed time, t, after the start of a run when the phase separation appears, is revealed in the case of a first-order reaction by a change in slope of ξ vs t. Because of this change in slope, any ξ vs t data, which are collected before the phase separation occurs, will fail to extrapolate to the observed equilibrium value of the extent of reaction. As the equilibrium is the reference state for the thermodynamic theory of critical effects,[23,24] we have ignored in a kinetic run any data which were collected prior to the occurrence of the phase transition

(3) Connection Between Kinetics and Thermodynamics. If the reaction in eq 1 is elementary, first order in the forward direction, and essentially irreversible, the net rate of reaction, $d\xi/dt$, is given by[5,8]

$$\frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi_e) \qquad (3)$$

where $1/\tau$ is the specific relaxation rate. Ordinarily, $1/\tau$ is taken be proportional of $(\partial\Delta G/\partial\xi)_e$, where ΔG is the Gibbs energy difference separating products from reactants, and the subscript, e indicates that the derivative is evaluated at equilibrium.[23,24] Application of transition state theory shows that

$$\frac{1}{\tau} = \frac{r'(\xi_e)}{RT}\left(\frac{\partial\Delta G}{\partial\xi}\right)_e \qquad (4)$$

where T is the absolute temperature, R is the ideal gas law constant, and $r'(\xi_e)$, is the rate of the forward reaction at equilibrium.[25] Starting with the condition $\xi = 0$ at $t = 0$, the integral of eq 3 is

$$\xi = \xi_e(1 - \exp(-t/\tau)) \qquad (5)$$

As T approaches T_c , the critical behavior of $1/\tau$ may depend on the thermodynamic factor, $(\partial\Delta G/\partial\xi)_e$ and/or upon the rate factor, $r'(\xi_e)$, in eq 4. Of these two factors, the effect of temperature on $(\partial\Delta G/\partial\xi)_e$ can be analyzed by invoking the Griffiths−Wheeler rules, which express the principle of critical point universality in terms of the critical behavior of thermodynamic derivatives.[26] By contrast, there does not seem to be a theory available for predicting the temperature behavior of $r'(\xi_e)$ under these same conditions.

Basing their arguments on the concept of critical point universality, Griffiths and Wheeler assert that the critical properties of multicomponent mixtures can be derived from the analogous properties of the liquid−vapor critical point of a pure fluid.[26] They begin by separating the thermodynamic variables into two classes. Forming the first class are the fields, such as the temperature, pressure, and the chemical potentials of the components. In a system at thermodynamic equilibrium, a field variable has a uniform value across all coexisting phases. Because it can be expressed as a linear combination of the chemical potentials of the reactants and the products, ΔG is a field. Forming the second class are the densities, which include the entropy, enthalpy, and composition variables (e.g., the mass fractions of the chemical components). A density variable has a unique value in each phase coexisting at equilibrium. The volume concentration variable, ξ, is a density.

The thermodynamic derivative, $(\partial \Delta G/\partial \xi)_e$, is thus the derivative of a field with respect to a density. According to Griffiths and Wheeler, when the experimental conditions are such that the fixed thermodynamic variables consist of fields and two or more densities, then the derivative of a field with respect to a density, such as $(\partial \Delta G/\partial \xi)_e$ should be a smooth function of the temperature as T approaches T_c; on the other hand, if fewer than two densities are held fixed, the derivative should go to zero as a power of $|T - T_c|$. If one density is held fixed, the derivative of a field with respect to a density is said to go to zero *weakly*.[26] This means that, when T approaches T_c, the derivative will be proportional to $|T - T_c|^x$, where the value of the exponent, x, depends on whether the critical point is approached along a path parallel or at an angle to the coexistence curve.[26,27] If parallel, x is identical to the pure fluid isochoric specific heat exponent,[14] $\alpha = 0.11$. If at an angle, x is equal to the ratio of exponents, $\alpha/\beta\delta = 0.070$, where $\beta = 0.326$ is the exponent that determines the shape of the liquid−vapor coexistence curve,[14] whereas $\delta = 4.80$ is the exponent that determines the shape of the liquid−vapor critical isotherm of the pure fluid.[14] When no densities are held fixed, the derivative of a field with respect to a density is said to go to zero *strongly*.[26] A derivative that goes to zero strongly is proportional to $|T - T_c|^x$, where the value of x is an order of magnitude larger than in the case of a weak critical effect. For a strong effect, when the direction of approach to the critical point is parallel to the coexistence curve, x is identical to the exponent, $\gamma = 1.239$, which characterizes the temperature dependence of the isothermal compressibility of a pure fluid;[14] when the direction of approach is at angle, x is equal to $1 - (1/\delta) = 0.792$. Thus, the application of the method of Griffiths and Wheeler to determine the critical behavior of $(\partial \Delta G/\partial \xi)_e$ for a chemical reaction at constant temperature and pressure in a binary solvent rests upon an examination of the experimental conditions that determine the number of fixed density variables.[6−8]

In addition to determining the reaction rate, the temperature dependence of the derivative, $(\partial \Delta G/\partial \xi)_e$, also determines the magnitude of the fluctuations in the concentrations of the reactants and products at chemical equilibrium. As $(\partial \Delta G/\partial \xi)_e$ goes to zero, oscillations in the extent of reaction, ξ, about its equilibrium value, ξ_e, grow in amplitude.[28] If these fluctuations were directly observed, one would presumably see the value of the extent of reaction pass through equilibrium back and forth between an excess of products and an excess of reactants.

3. Experiment

(1) Decomposition of Acetone Dicarboxylic Acid in Isobutyric Acid + Water (UCST). Our first attempts to decarboxylate acetone dicarboxylic acid in isobutyric acid + water proved fruitless. Fortunately, we subsequently discovered that Jencks has reported that primary amines catalyze the decomposition of beta keto acids, whereas secondary and tertiary amines have less of an effect.[29] In agreement with this claim, we observed that there was negligible decomposition of acetone dicarboxylic acid in triethylamine + water (LCST).[30] Following Wiig,[15] we found that the decomposition of acetone dicarboxylic acid in isobutyric acid + water could be effectively catalyzed by aniline.

Acetone dicarboxylic acid, aniline, and isobutyric acid were purchased from Aldrich and used as received. Water was once distilled from a glass system. The binary solvent mixture was prepared at the critical composition[31] of 38.8 mass % isobutyric acid by weighing. The UCST of the binary mixture was 26.2 °C. To a sample of the binary critical mixture was added 1.64 mL of aniline to make 100 mL of the ternary catalytic mixture. By observation of critical opalescence, the critical point of the ternary mixture was found to be $T_c^0 = 19.0$ °C. The volume of aniline added was just enough to establish a convenient half-life for the reaction but not so much as to force the critical temperature below the lowest feasible temperature for easy operation of the thermostat. When the ternary mixture was left standing at a temperature just below the critical temperature, a meniscus formed near the middle of the reaction cell. The appearance of the meniscus not only served to confirm the critical temperature but also by its position near the center served to demonstrate that the dissolved catalyst had little effect on the critical composition.[20−22] As the UCST of the ternary mixture was below the critical solution temperature (26.2 °C) of the binary mixture, the acid−base reaction between isobutyric acid and aniline served to increase the mutual miscibility of isobutyric acid and water.[1]

The reaction vessel was a 100 mL cylindrical glass flask with two necks, one of which was used to introduce the catalytic mixture, whereas the other was connected to the gas dilatometer. For a description of the gas dilatometer, see Appendix A. To start the reaction, enough acetone dicarboxylic acid was added to a sample of the ternary mixture in the reaction flask to make 100 mL of solution that had a reactant concentration of 0.007 M. The neck, through which the reactant was introduced, was sealed off. The reaction flask and dilatometer then formed a closed system isolated from the ambient atmosphere. The evolved carbon dioxide was captured and the amount determined as a function of time using the dilatometer. The liquid mixture in the flask was well stirred with a magnetically driven stirring bar. The flask was submerged in a 14 L water bath, the temperature of which was determined by a platinum resistance thermometer that was read using a 8 $^1/_2$ digit multimeter. To maintain temperatures above the laboratory ambient, the water bath was heated with a submerged, underwater light bulb. To achieve temperatures below ambient, the water bath contained a submerged coil of copper tubing through which chilled water was pumped from an adjoining ice chest. Power to the light bulb and to the pump was regulated by a Philadelphia Rotostat thermostat connected to a Cole Parmer 115 V variable output controller.

The overall stoichiometry of the decomposition of acetone dicarboxylic acid is

$$CO(CH_2COOH)_2(s) \rightarrow CO(CH_3)_2(s) + 2\ CO_2(g) \quad (6)$$

where the s in parentheses stands for solution phase and the g for gas phase.

After the reaction had gone to completion, and the liquid had come to equilibrium with the evolved carbon dioxide, the critical solution temperature was found to be $T_c = 18.9$ °C. The value of the coefficient, a, in eq 2 was thus −14.6 °C mol^{-1} L.

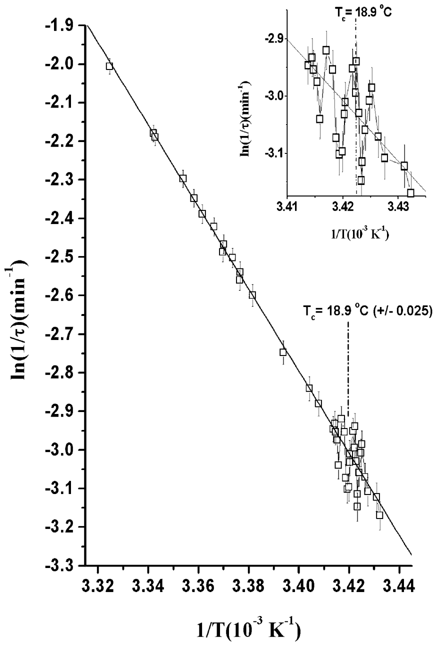

Figure 1. Specific relaxation rate, $1/\tau$ (pseudo first-order rate constant) as a function of the reciprocal of the absolute temperature, $1/T$, for the aniline catalyzed decomposition of acetone dicarbolylic acid in isobutyric acid + water. The upper critical solution temperature at chemical equilibrium was 18.9 °C. The insert to the main figure shows the data in the critical region in more detail.

Because the reaction mixture had the same composition at the start of each kinetics run, the value of the equilibrium critical temperature, $T_c = 18.9$ °C, was a constant for our experiment.

As indicated in the Appendix, the accumulation of CO_2 in the reaction vessel displaced water dropwise from a siphon that was part of the gas dilatometer. The displaced water was caught in a beaker placed on the pan of an analytical balance. The change in mass, $\Delta m(t)$, recorded by the balance was proportional to the extent of reaction, $\xi(t)$. By comparison with eq 5, the time dependence of the change in mass could be expressed as

$$\Delta m(t) = \Delta m_e(1 - \exp(-t/\tau)) \tag{7}$$

where Δm_e is the change in mass recorded at reaction equilibrium. In fitting mass vs time data to eq 7, Δm_e and the rate coefficient, $1/\tau$, were treated as free parameters.

In Figure 1, we show an Arrhenius plot of the temperature dependence of $1/\tau$. The units of τ are minutes. The straight line, which represents a fit of $\ln(1/\tau)$ vs $1/T$ data collected at temperatures far above T_c, has the equation

$$\ln(1/\tau) = 33.35 - 88\,400/RT \tag{8}$$

where $R = 8.314$ J K^{-1} mol^{-1} and T is the absolute temperature. The constant term on the right of eq 8 has a standard error of ±0.02, whereas the activation energy has a standard error of ±1200 J/mol. Beyond the uncertainty in each point as determined by its error bar, the values of $1/\tau$ shown in Figure 1 appear to make three complete oscillations about the interpolation of the Arrhenius line through the critical region. A numerical tabulation of the data appears in Table 1.

(2) Decomposition of Benzene Diazonium Tetrafluoroborate in 2-Butoxyethanol + Water (LCST). The organic component of the solvent, 2-butoxyethanol, was purchased from Aldrich and used as received. Benzene diazonium tetrafluoroborate was synthesized fresh following the method of Dunker, Starkey, and Jenkins.[32] The binary solvent mixture was prepared at the critical composition, 24.78 mass % 2-butoxyethanol[33] by weighing. The LCST of the binary mixture was $T_c^0 = 50.178$ °C. At the start of each kinetics run, 0.1512 g of dry benzene diazonium tetrafluoroborate was added to 125 mL of the solvent mixture.

TABLE 1: Specific Relaxation Rate, 1/τ (Pseudo-First-Order Rate Constant) as a Function of the Centigrade Temperature, *T*, for the Aniline Catalyzed Decomposition of Acetone Dicarboxylic Acid in Isobutyric Acid + Water[a]

T (°C)	$1/\tau$ (min^{-1})	T (°C)	$1/\tau$ (min^{-1})
18.20	0.0420	19.64	0.0511
18.30	0.0441	19.70	0.0522
18.60	0.0447	19.72	0.0533
18.70	0.0464	19.78	0.0525
18.80	0.0505	20.28	0.0561
18.83	0.0494	20.60	0.0584
18.90	0.0469	21.50	0.0641
18.95	0.0444	22.57	0.0744
18.96	0.0430	22.99	0.0789
19.00	0.0483	23.01	0.0773
19.03	0.0529	23.27	0.0819
19.05	0.0501	23.57	0.0849
19.10	0.0522	23.60	0.0831
19.21	0.0493	23.92	0.0888
19.22	0.0482	24.32	0.0918
19.25	0.0452	24.62	0.0956
19.30	0.0450	25.00	0.1005
19.35	0.0463	26.00	0.1119
19.40	0.0522	26.05	0.1131
19.50	0.0539	27.62	0.1345
19.60	0.0478		

[a] The upper critical solution temperature at chemical equilibrium was 18.9 °C.

The overall stoichiometry of the benzene diazonium tetrafluoroborate decomposition reaction is

$$C_6H_5N_2BF_4(s) + H_2O(s) \rightarrow C_6H_5OH(s) + HBF_4(s) + N_2(g) \tag{9}$$

The rate of evolution of nitrogen was determined by collecting the nitrogen in the gas dilatometer. The kinetics were first order in the concentration of the benzene diazonium ion. The change in mass of the water displaced by the gas was registered by the balance and was fitted as a function of time to eq 7 with Δm_e and $1/\tau$ treated as free parameters. Although dimly visible through the violet color of the solution, critical opalescence was sufficiently distinct to permit the equilibrium critical temperature to be estimated as $T_c = 49.3$ °C; thus, the value of the coefficient a in eq 2 was -139 °C mol^{-1} L.

In Figure 2, we show an Arrhenius plot of the temperature dependence of $1/\tau$. The straight line, which represents a fit of $\ln(1/\tau)$ vs $1/T$ data collected at temperatures below T_c, has the equation

$$\ln(1/\tau) = 33.14 - 95\,700/RT \tag{10}$$

The constant term on the right had a standard error of ±0.02, whereas the activation energy had a standard error of ±1600 J/mol. None of the data near the critical temperature departs significantly from the Arrhenius line, and no critical effect is apparent.

(3) Decomposition of Ethyl Diazoacetate in Isobutyric Acid + Water (UCST). The binary solvent mixture was prepared at the critical composition of 38.8 mass % isobutyric acid[31] by weighing. The UCST of this mixture was $T_c^0 = 26.12$ °C. Ethyl diazoacetate was purchased from Aldrich and used as received. To start each kinetics run, 7.14 μL of ethyl diazoacetate were added to 100 mL of the solvent mixture.

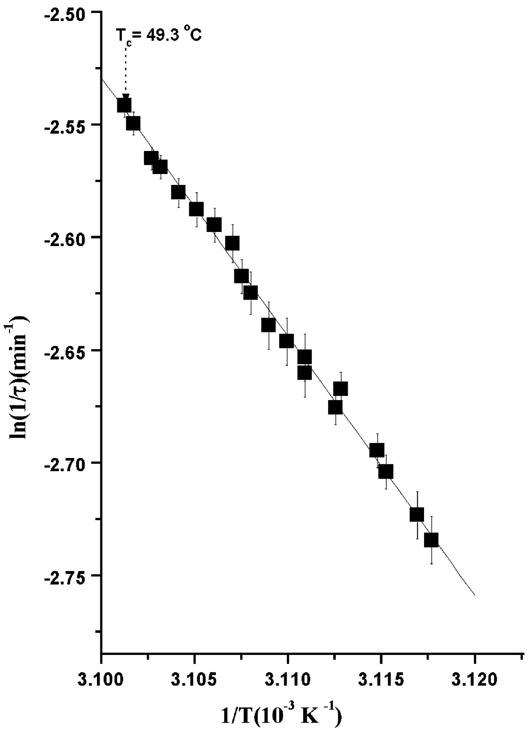

Figure 2. Specific relaxation rate, $1/\tau$(first-order rate constant) as a function of the reciprocal of the absolute temperature, $1/T$, for the decomposition of benzene diazonium tetrafluoroborate in 2-butoxyethanol + water. The lower critical solution temperature at chemical equilibrium was 49.3 °C.

The overall stoichiometry of the ethyl diazoacetate decomposition reaction is

$$N_2CHCOOC_2H_5(s) + H_2O(s) \rightarrow HOCH_2COOC_2H_5(s) + N_2(g) \quad (11)$$

The rate law was first order in the concentration of ethyl diazoacetate. The rate of reaction was followed using the gas dilatometer. The time dependence of the mass of water displaced by the nitrogen gas was recorded by the balance and fitted to eq 7. After the reaction had come to equilibrium with the evolved nitrogen, the critical temperature was found to be $T_c = 26.10 \pm 0.03$ °C; the value of the coefficient, a, in eq 2 was essentially zero.

In Figure 3, we show an Arrhenius plot of the temperature dependence of $1/\tau$. The units of τ are minutes. The straight line, which represents a fit of $\ln(1/\tau)$ vs. $1/T$ data collected at temperatures far above T_c, has the equation

$$\ln(1/\tau) = 27.77 - 78\,600/RT \quad (12)$$

The constant term on the right had a standard error of ±0.02, whereas the standard error in the activation energy was ±400 J/mol. The data do not appear to deviate from background in the critical region, and no critical effect is apparent.

4. Discussion and Conclusions

(1) Acetone Dicarboxylic Acid. Aniline is thought to accelerate the decarboxylation of beta keto acids, such as acetone dicarboxylic acid, by attacking the keto group to form a carbinolamine.[29] In the next step of this mechanism, the carbinolamine releases a molecule of carbon dioxide in a unimolecular reaction that involves a pericyclic interchange of σ and π bonds.[29] The overall rate is proportional to the product of the concentrations of both aniline and acetone dicarboxylic acid. Given that the aniline is not consumed in the reaction, the rate law is psuedo-first-order, as we have observed.

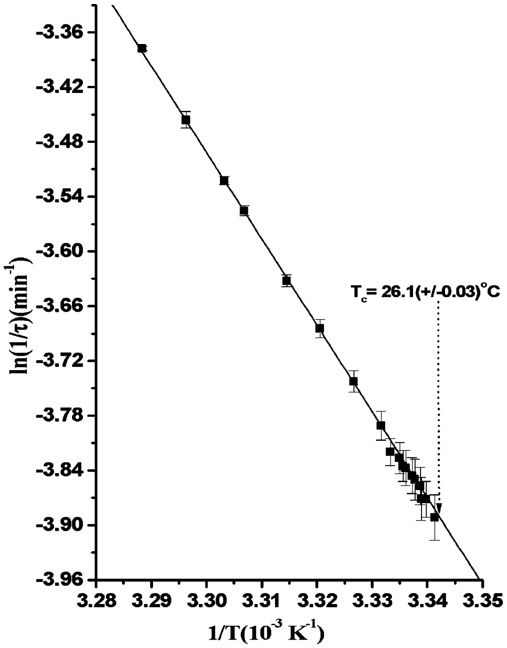

Figure 3. Specific relaxation rate, $1/\tau$ (first-order rate constant) for the decomposition of ethyl diazoacetate in isobutyric acid + water. The upper critical solution temperature at chemical equilibrium was 26.10 °C.

At 25 °C, the acid ionization constant of isobutyric acid[34] is $K_a = 1.416 \times 10^{-5}$, the base ionization constant of aniline[35] is $K_b = 3.945 \times 10^{-10}$, and the ionization constant of water is $K_w = 10^{-14}$. The equilibrium constant for the acid−base reaction between isobutyric acid and aniline to produce anilinium ion and isobutyrate ion is $K = K_aK_b/K_w = 0.5586$. The concentrations of isobutyric acid and aniline in the catalytic mixture as prepared were 4.40 and 0.18 M, respectively. Calculation using $K = 0.5586$ showed that the concentrations of isobutyric acid and aniline remaining after the acid−base reaction had come to equilibrium were 4.24 and 0.012 M, respectively. Some free aniline thus remained to catalyze the decarboxylation reaction. The isobutyrate ion, which was produced at a concentration of 0.17 M by the acid−base reaction, combined with the remaining isobutyric acid to form an unbalanced buffer solution, the pH of which was calculated to be 3.4. In estimating this pH value, we have ignored the lesser effect of the ionization of the carbonic acid which is produced by the dissolution of carbon dioxide formed as a product in eq 6. The above considerations serve to identify the components introduced into the mixture by side reactions.

Although the decomposition of acetone dicarboxylic acid is an heterogeneous reaction, a Griffiths−Wheeler analysis[26] can still be applied to the rate law. Because our gas dilatometer was closed with a flexible plastic bag, the total gas pressure over the reacting liquid mixture was fixed at one atmosphere. The thermostat controlled the temperature. Thus, having accounted for the fixed values of the fields, P and T, the thermodynamic variables still remaining to be considered are all densities. These density variables are the mass fractions of acetone dicarboxylic acid, acetone, carbon dioxide, aniline, isobutyric acid, water, and their reaction products. Because acetone dicarboxylic acid, acetone, and carbon dioxide are each involved in the stoichiometry of the reaction in eq 6, their mass fractions at chemical equilibrium depend on both P and T and cannot be independently fixed. Moreover, because the reaction in eq 6 occurs simultaneously with the acid−base equilibrium involving isobutyric acid and aniline and the reaction of carbon dioxide with water, the equilibrium mass fractions of aniline, isobutyric acid, and water and their reaction products must all be functions of temperature and pressure. Consequently, as there are no density variables held fixed, the rules of Griffiths and Wheeler predict that the value of $(\partial \Delta G/\partial \xi)_e$ should go to zero strongly as $T \rightarrow T_c$. On the basis of eq 4, we thus conclude that the rate of decarboxylation of acetone dicarboxylic acid should slow in the critical region.

If one employs an Arrhenius line as a measure of the noncritical background, Figure 1 shows that instead of just slowing down, as would be predicted on the basis of eq 4, the experimental values of $1/\tau$ in the critical region exhibit three repetitions of a cycle of slowing down followed by speeding up. By comparison, we have observed only a single cycle of this behavior in the case of S_N1 reactions not involving gas evolution.[6,7]

The introduction of a catalyst to accelerate the rate of a reaction near a critical point of solution is not new. Becker and collaborators[3] started with a mixture of acetic anhydride + 1,2-ethanediol at its consolute composition. They added trifluoroacetic acid to catalyze the reaction of the two solvent components to produce the 1,2-ester of ethanediol and acetic acid. Following the extent of reaction of this catalyzed mixture by calorimetery, Becker *et al.* reported a decrease in the rate of heat evolution near the consolute point. They associated this shift in heat evolution rate with a slowing down in the net rate of reaction of the solvent pair.[3]

(2) Benzene Diazonium Tetrafluoroborate. The mechanism of decomposition of benzene diazonium tetrafluoborate is S_N1.[16] Because we employed a temperature thermostated gas dilatometer to measure the rate, the fixed field variables were P and T. There are six chemical components to be considered in the reaction mixture. Of these, benzene diazonium tetrafluoroborate, water, phenol, nitrogen, and fluoroboric acid appear in eq 9. Water serves as both a reactant and as a solvent component. The remaining solvent component, 2-butoxyethanol, would appear to be inert in the sense that it does not participate in any chemical reaction involving the other components in eq 9. We can rule out, for example, any substantial acid−base reaction between fluoroboric acid and 2-butoxyethanol in an aqueous mixture, because the 2-butoxyethanol is a much weaker base than water.[36] In the absence of known reactions involving 2-butoxyethanol, we suggest that its concentration should serve as a fixed density variable. Consequently, with one density variable fixed, we can expect any deviation in the values of $1/\tau$ from background in the critical region to be proportional to $|T - T_c|^x$, where x is either of the weak exponents, $\alpha = 0.11$ or $\alpha/\beta\delta = 0.070$, depending upon the direction of approach to the critical point.

In our previous experiments with reactions in binary solvents with a critical point,[4−8] a change in $1/\tau$ could be easily observed over the experimental width of the critical region, which was about $|(T - T_c)/T_c| = 3 \times 10^{-3}$. By contrast, if the ratio, $|(T - T_c)/T_c|^x$ with $x \approx 0.1$, were to change by this amount, the value of T would have to approach T_c within 5×10^{-23} K. Since the ability of our experimental apparatus to control temperature is about 1 mK, we had little sensitivity to observe a weak critical effect in the net rate of reaction in this reaction mixture. The data plotted in Figure 2 confirm this conclusion, since no critical effect in $1/\tau$ is anywhere apparent. By comparison, had we carried out the decomposition of benzene diazonium tetrafluoroborate in triethylamine + water (LCST), a strong critical effect might have been expected, because the acid−base equilibrium between HBF_4 and triethylamine would have tied up the nonaqueous component of the solvent, and the mixture would have contained no inert components.

(3) Ethyl Diazoacetate. We chose isobutyric acid + water as the solvent, because the decomposition of ethyl diazoacetate is catalyzed by H^+.[19] The first step in the reaction mechanism is the rapid transfer of a proton from H_3O^+ to ethyl diazoacetate to form the cation, $N{\equiv}N^+{-}CH_2COOC_2H_5$, which subsequently releases a molecule of nitrogen in a slow, unimolecular reaction. The carbocation produced by this reaction immediately attacks water to form ethyl hydroxyacetate.[18]

The reactants in eq 11 are ethyl diazoacetate and water, whereas the products are ethyl hydroxyacetate and nitrogen. The remaining solvent component, isobutyric acid, does not react with any of the components in eq 11. For example, because no strong acid catalyst is available, isobutyric acid cannot undergo a transesterification reaction with ethyl hydroxyacetate. Based upon the limited sensitivity of our experimental apparatus to a weak critical effect, as discussed above, the absence of any visible critical slowing down or speeding up in the Arrhenius plot in Figure 3 would seem to indicate that this mixture contains at least one effectively inert component, which is probably isobutyric acid.

(4) Conclusions. The acetone dicarboxylic acid rate data shown in Figure 1 answer in the affirmative the question that we posed in the Introduction, namely, a critical rate effect can be detected in a heterogeneous reaction by following the extent of reaction using a method other than the measurement of the conductivity of the liquid. When taken in combination, the results summarized in Figures 1−3 suggest that the effect can be observed so long as the mixture contains no inert components. It is worth noting that in contrast to other first order reactions, which we have previously investigated for critical effects,[4−7] the decomposition reaction of acetone dicarboxylic does not proceed by the S_N1 mechanism.

The influence of the consolute point of a binary liquid mixture on the equilibrium solubility of a gas has yet to be investigated. Thus, in the case of the decomposition of acetone dicarboxylic acid, we cannot be absolutely sure that the oscillations shown in Figure 1 represent the direct action of the critical point on $1/\tau$ or the indirect action of some critical effect in the solubility of carbon dioxide on the net rate of reaction. Both possibilities should probably be considered kinetic effects, however, because in the case of this heterogeneous reaction, the dissolution of a gaseous product can perhaps be considered as an integral part of the overall reaction mechanism.

Assuming that the observed critical effect is associated with $1/\tau$, it would appear that the application of the Griffiths−Wheeler rules to the critical behavior of the thermodynamic derivative, $(\partial \Delta G/\partial \xi)_e$, is insufficient by itself to account for the cyclic behavior seen in Figure 1. Consequently, we may hereafter have to look to the critical behavior of the dynamic factor $r'(\xi_e)$ or other causes for an explanation.

To begin this search, the several versions of crossover theory come to mind.[37−45] Crossover models endeavor to formulate an equation of state that includes divergent thermodynamic derivatives in the critical region but exhibits analytic behavior far from the critical point. Instructive in this regard is the crossover model for the van der Waals equation of state developed by Wyczalkowska et al.[45] Although the van der Waals equation of state correctly reduces to the ideal gas law at sufficiently low densities, it predicts a nonphysical cubic behavior of the properties of the gas in the critical region. Wyczalkowska et al. construct a Helmholtz free energy that successfully corrects for this cubic behavior. By comparison, the reactants, catalysts, and products in our experiments form with the solvent components a dilute, perhaps even ideal solution when the conditions place the system far from the critical region. By the introduction of an appropriate correction to this ideal behavior, a crossover model could perhaps be constructed that accounts for the oscillations in $1/\tau$ that we have observed in the critical region.

Our three heterogeneous reactions are not the first of this class to be studied near a consolute point. Greer and collaborators[46] observed the position of chemical equilibrium in the dimerization of NO_2 to form N_2O_4 near the critical point of a solution of perfluoromethylcyclohexane + carbon tetrachloride (UCST). Because the mixture was confined in a closed container with space above the liquid to accommodate the vapors of volatile components, such as NO_2 and N_2O_4, the reaction was heterogeneous. The position of equilibrium was monitored by making measurements of the dielectric constant of the liquid phase. Greer et al.[46] reported a 4% shift in the position of equilibrium toward the side of NO_2 as the temperature approached the critical value.

We are aware that Morrison has urged caution in automatically associating a change in the physical properties of a solution near a critical point with the effect of a chemical reaction.[47] He pointed out, for example, that critical opalescence can interfere with measurements of changes in optical density. Subsequently, Greer showed that, due to the critical slowing down of thermal conductivity, thermal conductivity probes are not reliable measures of the extent of reaction near the liquid−vapor critical point.[48] Where possible, the simplest way to avoid such competing effects in experiments with binary liquid solvents near a critical point may be to take aliquots from the well-stirred mixture. After a temperature change or dilution of the aliquot, the solute concentration can be determined by standard methods of analytical chemistry under conditions that are far from the critical point.

Finally, to put our results into perspective, we note that, in binary liquid mixtures, slowing down has been reported in measurements of the ionic conductivity,[7,49] the diffusivity,[50,51] and the fluidity (reciprocal of the Newtonian viscosity).[51] Speeding up, on the other hand, has been reported in measurements of the rate of dielectric relaxation.[52] By contrast, the coexistence of slowing down and speeding up, as illustrated in Figure 1, has only been reported in the case of measurements of the rate of chemical reaction.[6,7]

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Appendix: Theory of the Gas Dilatometer

To measure the rate of a reaction involving gas evolution, the gas dilatometer diagrammed in Figure 4 was connected at point A to a closed reaction vessel containing the reaction mixture and air. In the figure, the end of the gas inlet tube, AT, at T was tightly connected to a flexible, thin-walled polyethylene sack, S, in the air space of the tightly stoppered bottle, B. The reaction vessel, tube, and sack formed a gastight volume, the sack preventing direct contact between the gas evolved by the reaction mixture and the contents of the bottle. The lower half of the volume of the bottle contained water, whereas the upper half of the volume contained air. The tube, BC, was filled with water and together with the bottle formed a siphon. As the gas produced in the reaction vessel entered the sack, the sack expanded against the air in the bottle. The change in pressure forced water through the siphon tube BC. The liquid displaced from the siphon tube at C was caught in a beaker on the pan of the analytical balance (not shown). The increase in mass registered by the balance was recorded by a personal computer. We will show that the increase in mass was proportional to the instantaneous value of the number of moles of gas produced.

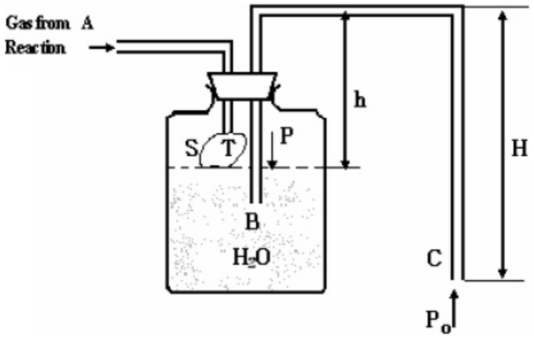

Figure 4. Schematic diagram of the gas dilatometer used to follow the rate of gas evolution reactions. The reaction vessel is connected to the glass tube at *A*. The gas evolved as a product of the reaction in the reaction vessel enters at *A* and travels through the glass tube, AT, to the flexible polyethylene sack, *S*, at *T*. The tightly stoppered bottle is partially full of water and forms a siphon with the water-filled glass tube connecting *B* to *C* against the external air pressure, P_0. Whereas the height, *H*, remains constant, the height, *h*, increases as the gas fills the sack. Water expelled from the siphon at *C* is caught in a beaker on the pan of an analytical balance and weighed. The change in mass recorded by the balance is stored by a personal computer. The change in mass is proportional to the extent of reaction.

For there to be no flow through the siphon tube, the total pressure inside the bottle at the water surface should equal the total pressure at the outlet, C. At C, in addition to the atmospheric pressure, P_0, there is hydrostatic pressure, ρgH, where ρ is the density of water, g is the acceleration due to gravity, and H is the hydrostatic head. The total pressure at C is $P_0 - \rho gH$. The minus sign appears because the air pressure and the hydrostatic pressure act in opposite directions. Inside the bottle, the pressure at the water surface is made up of the pressure exerted by the evolved gas, P, and the hydrostatic pressure, ρgh. The total pressure is $P - \rho gh$. For there to be no flow at C, we must have

$$P - \rho gh = P_0 - \rho gH \qquad \text{(A.1)}$$

According to eq A.1 and the ideal gas equation of state

$$P = \frac{nRT}{V} = P_0 - \rho g(H - h) \qquad \text{(A.2)}$$

where n is the number of moles of gas in the volume, V, which includes the reaction vessel and the sack.

We let the subscript 1 represent conditions at the start of the reaction and the subscript 2 represent conditions after a certain amount of gas has been evolved. Using eq A.2 to represent the change in pressure, we obtain

$$P_2 - P_1 = RT\left(\frac{n_2}{V_2} - \frac{n_1}{V_1}\right) = \rho g(h_2 - h_1) \qquad \text{(A.3)}$$

If A is the inside cross sectional are of the bottle, the change in gas volume is

$$V_2 - V_1 = A(h_2 - h_1) \tag{A.4}$$

We next let $\Delta V = V_2 - V_1$, $\Delta n = n_2 - n_1$and substitute eq A.4 into eq A.3. The result is

$$\frac{\rho g}{A}\Delta V = RT\left(\frac{n_1}{V_1}\right)\left[-1 + \frac{1 + (\Delta n/n_1)}{1 + (\Delta V/V_1)}\right] \tag{A.5}$$

The denominator within the brackets can be expanded for small values of $\Delta V/V_1$ in a geometric series. Retaining only terms first order in the small quantities, $\Delta V/V_1$ and $\Delta n/n_1$, we can solve for Δn in terms of ΔV. The result is

$$\Delta n = \frac{P_1 \Delta V}{RT}\left[1 + \frac{\rho g V_1}{P_1 A}\right] \tag{A.6}$$

Since the change in mass, Δm, recorded by the balance equals $\rho\Delta V$, eq A.6 can be used to obtain

$$\Delta n = \frac{P_1 \Delta m}{\rho RT}\left[1 + \frac{\rho g V_1}{P_1 A}\right] \tag{A.7}$$

This demonstrates that the change in number of moles of gas in the reaction vessel is proportional to the change in mass recorded by the balance. In addition to the constants, $\rho = 1$ g/cm^3, $g = 980$ cm/s^2, our apparatus had $A = 176$ cm^2, $V_1 = 500$ cm^3, and since P_1 differed little from one atmosphere, we computed $\rho g V_1/P_1 A = 3 \times 10^{-3}$; hence, the quantity within the bracket in eq A.7 was close to unity.

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