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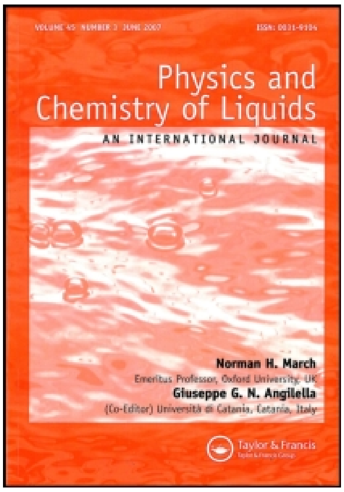

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# How Might Chemical Reaction Rates in Solution Be Affected By Intense Density Fluctuations of the Solvent?

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# HOW MIGHT CHEMICAL REACTION RATES IN SOLUTION BE AFFECTED BY INTENSE DENSITY FLUCTUATIONS OF THE SOLVENT?

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A chance observation of the great solvation power of fluid xenon in the critical state, has led us to the suggestion that a reaction between two relatively nonpolar molecules to form a more polar product, will have a higher rate constant in the critical fluid of xenon than in the noncritical fluids at 1 K above or below $T_c$. The large density fluctuations in the highly compressible critical fluid enhance the solvation of the dipolar transition state, through dipole-induced-dipole attractions. This is predicted to lower the activation energy of the reaction and increase the reaction rate. An example is $1\text{-}C_4H_8 + Br_2 \rightarrow C_4H_8Br_2$, in the dark.

*Keywords:* Critical fluid; density fluctuations; reaction rate enhancement

Much work has been done on solvated electrons in nonpolar solvents as a function of thermodynamic state [1]. Behavior in the critical fluid of xenon was especially well studied [2, 3], because of the relative ease of attaining extremely pure xenon, and the ready accessibility of the critical temperature of xenon, 289.79 K, and the non-difficult containment of the critical pressure, 5.83 MPa [4]. GRF and coworkers noticed that when a newly manufactured conductance cell was used, the stainless steel electrodes looked particularly shiny after it had contained the critical fluid of xenon for a few hours. We concluded that critical xenon is an exceptionally good solvent for polar materials,

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probably because of its high electronic polarizability and the large density fluctuations that occur in the critical fluid.

We propose here that the solvation power of critical fluids should accelerate reactions of less-polar reactants that form more-polar products. The acceleration should be observable in a narrow temperature range of $< 1$ K, on approaching the critical fluid from below or above the critical temperature.

Potentially interesting solvents that have readily accessible critical states are listed in Table I. The selection in Table I was made on the bases that $T_c$ is near room temperature and $P_c < 10\,\mathrm{MPa}$.

Xenon, already referred to above, is an extensively studied liquid. Figure 1 reproduces the velocity of sound in the coexistent liquid and vapor near the critical region, and in the gas at the critical density above $T_c$ [4]. The cusp in the velocity of sound illustrates the narrowness of the region around the critical point where accelerated reaction rates might be observed. We except this to be the case not only for xenon, but also for the other fluids listed in Table I.

To make a specific proposal of an experiment worthy of experimental investigation, we consider briefly the case of 1-butene reacting with a halogen, say $Br_2$.

$$CH_3CH_2CH = CH_2 + Br_2 \rightarrow CH_3CH_2CHBrCH_2Br \qquad (1)$$

The dipole moments of these reactants and products are listed, along with others, in Table II.

All of the materials need to be highly purified in a vacuum line, and transferred by low-temperature distillation. Small amounts of bromine and 1-butene should be added to a much larger amount of xenon in a reaction vessel that contains optical windows. The amount of xenon must correspond to the critical density when all of it is gaseous. The

TABLE I Potential solvents for studies of reaction rates in the critical state [a]

| *Solvent* | *mp (K)* | $T_c$ *(K)* | $P_c$ *(MPa)* |
|---|---|---|---|
| $CO_2$ | 217 | 304 | 7.3 |
| $N_2O$ | 182 | 310 | 7.2 |
| $SiH_4$ | 88 | 270 | 4.8 |
| $SiF_4$ | 183 | 259 | 3.7 |
| Xe | 161 | 290 | 5.8 |

[a] CRC Handbook of Chemistry and Physics, (1990), Weast R. C. (Ed.), CRC Press, Boca Raton, FL, USA, 70th edn.

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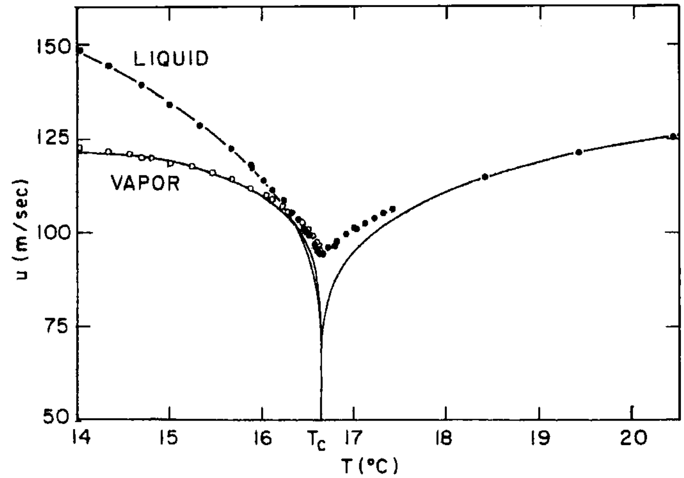

FIGURE 1 Sound velocity in xenon in the coexistent liquid and vapor phases near the critical state, and along the critical isochore for supercritical temperatures. The sound frequency is 1 M cy/s. The calculated thermodynamic values $u(0)$ are represented by solid lines.

TABLE II Molecular dipole moments [a]

| | ($10^{-30}$ $C \bullet m$) |
|---|---|
| $Br_2$ | 0.0 |
| $Cl_2$ | 0.0 |
| $I_2$ | 0.0 |
| $CH_3CH_2CH = CH_2$ | 1.1 |
| $CH_3CH_2CH_2CH_2Br$ | 6.9 |
| $CH_3CH_2CH_2CH_2Cl$ | 6.8 |
| $CH_3CH_2CH_2CH_2I$ | 7.1 |
| $CH_3CH_2CHBrCH_3$ | 7.4 |
| $CH_3CH_2CHClCH_3$ | 6.8 |
| $CH_3CH_2CHBrCH_2Br$ | ~ 10.0[b] |
| $CH_3CH_2CHClCH_2Cl$ | ~ 10.0[b] |
| $CH_3CH_2CHICH_2I$ | ~ 10.0[b] |

[a] Nelson, R. D. Jr., Lide, D. R. Jr. and Maryott, A. A. (1967). *NSRDS-NBS*, **10**, U. S. Gov't. Printing Office, Washington, D. C., USA.

[b] Extrapolated, by comparison with values for 1-$C_4H_9Br$, 2-$C_4H_9Br$, 1-$C_4H_9Cl$, 2-$C_4H_9Cl$, $C_6H_5Cl$, and *o*-$C_6H_4Cl_2$.

mixture should be kept frozen at liquid nitrogen temperature until the vessel has been sealed and placed in an apparatus from which all light can be excluded, and the interior of which can be accurately thermostated. The rate of reaction can be followed by suitably spaced

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microsecond pulses of light at the wavelength of an absorption maximum of $Br_2$, measured in a spectrophotometer.

Reaction (1) occurs slowly in the dark. Light accelerates the reaction by dissociating $Br_2$ molecules, and must be excluded. The product, and therefore the transition state, of reaction (1) is much more polar than are the reactants (Tab. II). The cusp in the speed of sound (Fig. 1) is related to an opposite cusp in the compressibility of the fluid [4]. The relatively large polarizability of xenon molecules and the large compressibility of the critical fluid will cause, we suggest, a stronger solvation of the transition state and reaction product. The solvation forces are dipole-induced-dipole attraction. Stronger solvation of the transition state should reduce the activation energy of the reaction, thereby increasing the rate.

It is interesting that an increase of rate is predicted upon approaching the critical temperature from above as well as from below. The temperature range of interest is only about 1 K on either side of $T_c$.

Similar experiments could be done with chlorine or iodine in place of bromine, and with other unsaturated hydrocarbons.

While the main purpose of this Letter is to propose a rather specific experiment to attempt to answer the question posed in the title, we conclude by remarking that, should such an experiment prove to expose salient features of reaction rates, it would be of importance to attempt to relate these to (a) the reactant – solvent interaction, and (b) the dynamic structure factor $S(k, \omega)$ of the solvent.

A natural first step might be to seek a possible correlation of the reaction rate with the long wavelength limit $k \to 0$ of $S(0)$, the static structure factor. It is known from fluctuation theory that $S(0)$ is related to the isothermal compressibility $\kappa_T$ through

$$S(0) = \rho k_B T \kappa_T, \tag{2}$$

where $\rho$ is the atomic number density and $k_B$ is Boltzmann's constant. However, since the experiment is concerned with rates, the adiabatic compressibility $\kappa_S$ is more appropriate than is $\kappa_T$. Since the heat capacities are in the relation $C_p \gg C_v$ as the critical point is approached, major differences arise between $\kappa_T$ and $\kappa_S$, and one requires information about $S(k, \omega)$.

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[3] Huang, S. S.-S. and Freeman, G. R. (1978). *J. Chem. Phys.*, **68**, 1355.

[4] Thoen, J. and Garland, C. W. (1974). *Phys. Rev. A*, **10**, 1311.

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