PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Thermal dependence of the characteristic time of a chemical reaction

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(Received 1 March 1993)

We report the temperature dependence of the chemical reaction characteristic time of crotonaldehyde and methylcyclohexane detected previously at room temperature [Phys. Rev. A **41**, 6 (1990)]. As with measurements effectuated by ultrasound techniques, we found an Arrhenius law for the temperature dependence of the characteristic time. Good agreement with known thermal and transport coefficients was found. The accuracy of the determination of the activation energy with the Rayleigh-Brillouin scattering technique is much more precise than with ultrasound techniques.

PACS number(s): 82.60.Hc, 44.60.+k, 78.35.+c, 82.20.Pm

I. INTRODUCTION

In a previous paper [1], we showed that the Rayleigh-Brillouin scattering technique is a good method to detect the relaxation time associated with a simple chemical reaction in a fluid between two forms A and B. We showed indeed that the width of the central Rayleigh line of the polarized (vertical-vertical, *VV*) spectra scattered by the fluid includes a part dependent on the square of the wave vector q and a wave-vector-independent part, this last part bringing with good precision the inverse of the relaxation time. In the previous paper we also presented experimental Rayleigh-Brillouin spectra of crotonaldehyde, methylcyclohexane, and acroleine at room temperature. We found that the relaxation times we measure are in good agreement with the classical ultrasound measurements.

We were able to interpret our result in terms of a contribution due to the coupling of hydrodynamic modes with a chemical-reaction process. The coupling mechanism occurs because the concentration fluctuations between the two species change with creation or annihilation of each kind of molecule.

We believe we were able to study these simple chemical reactions between two conformational isomers because the fluctuations in concentration of the fluid due to the chemical changes are strong enough to disturb the usual hydrodynamic behavior of the fluid. The theoretical framework for this interpretation was developed by Lallemand and Allain [2], starting from the general framework developed by Mountain [3]. In [1] we did the analysis of the room-temperature results with an adaptation of the calculation of Lallemand and Allain for the thermal-fluctuation case. Their initial model was proposed for forced Rayleigh scattering.

The absence of significant concentration fluctuations in previous Rayleigh-Brillouin-scattering studies of chemical reactions, is a possible explanation of the paucity of previous experimental results [4].

In this paper, we present experimental Rayleigh-Brillouin spectra for crotonaldehyde and methylcyclohexane in the temperature range 20–70 °C. We used the method described in [1] to analyze our data: we use a numerical simulation of the model we have developed in the framework of the hydrodynamic theory, taking into account the effect of the apparatus function (see Sec. II) by a numerical calculation of the convolution of the theoretical spectra.

For this calculation we use the temperature derivative of the quantity A, defined as the affinity of the chemical reaction. As stated in [1], this affinity is defined by

$$A=(RT/M)[\ln(x)-\ln(1-x)] .$$

Here T is the temperature, M the molecular mass, R the gas constant, and x is the molar fraction.

The derivative of the affinity can be represented by $(dA/dT)=(A/T)-K(T)$, where $K(T)$ is a weakly temperature-dependent function which can change with the temperature variation of the molar fraction x. The fit of the experimental spectra is obtained by adjustment of this parameter in the spectra. The temperature variation of the thermal conductivity, the density, and the heat capacity are introduced in the numerical calculation according to the available data [5–10]. It is important to note that the Brillouin width of the spectra is essentially controlled by shear- and bulk-viscosity contributions. Also the mutual diffusion is not easily detected in liquids and the thermal diffusivity has weak effects in the sound absorption term for the kind of fluid studied in this work.

We present the experimental setup in the second section. The experimental results and discussion will close this work.

II. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup is essentially the same as the one described previously for the room-temperature experiments. In this section we will give a short description and more details, essentially about the thermal-regulation procedure and some details about the experimental procedure.

1063-651X/93/48(4)/2695(4)/$06.00

As said previously [11], the optical elements of the scattering device are on a marble table, mechanically insulated from the vibrations of the building. The Spectra Physics 2020 argon laser and the double-pass plan Fabry-Pérot interferometer are also mechanically insulated from the marble. In fact we have detected, in some conditions, that the vibrations of the head of the laser (due to the heating of the water circulation needed for the cooling of the tube) create significant vibrations that we detected with the Fabry-Pérot interferometer. The sample is in the center of a cylindrical device, filled by a heating fluid; a set of pairs of parallel faces ensures a good transmission of the incident and scattered light across the heating system. The preparation of the fluid, with the highest-purity Aldrich product, includes triple distillation under vacuum and storage in a sealed tube.

The piezoelectric scanned interferometer gives a large amount of spectral information. This original procedure consists of the acquisition of the scattered intensity in 1024 channels, divided into two parts. The first part (the first 200 channels) contains the apparatus function, centered in the hundredth channel, while the second part contains the scattered spectra. The procedure, based on the combination of the rotation of two choppers, allows us to obtain the full scattered spectra, the experimental apparatus function, and the zero-intensity level of the scattered light. The information collected in a computer is analyzed with FORTRAN programs developed in the laboratory.

III. RESULTS AND DISCUSSION

We choose to study two fluids presenting conformational isomers with boiling and fusion points adapted to our experimental range of temperatures, in order to avoid perturbations in the vicinity of the phase changes.

The crotonaldehyde and methylcyclohexane studies give a large amount of information about the kinetics of the chemical reaction at equilibrium. In Figs. 1 and 2 we plot examples of a wave-vector dependence of each fluid at different temperatures and in Figs. 3 and 4 we

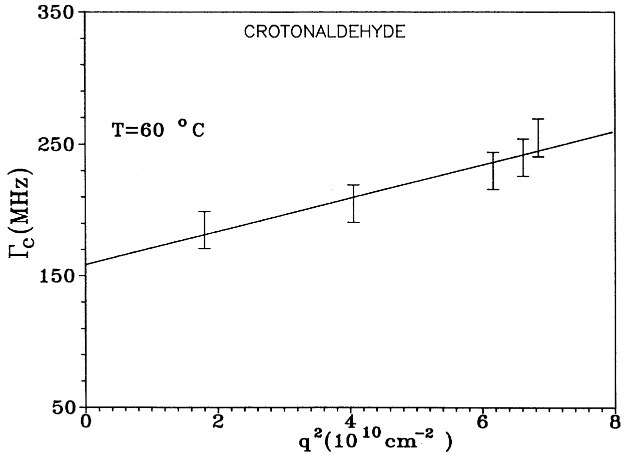

FIG. 1. Wave-vector variation of the half width at half height of the polarized Rayleigh line of crotonaldehyde at 60 °C.

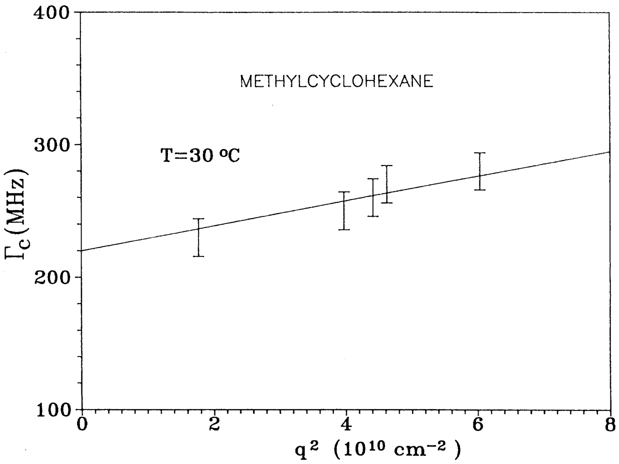

FIG. 2. Wave-vector variation of the half width at half height of the polarized Rayleigh line of methylcyclohexane at 30 °C.

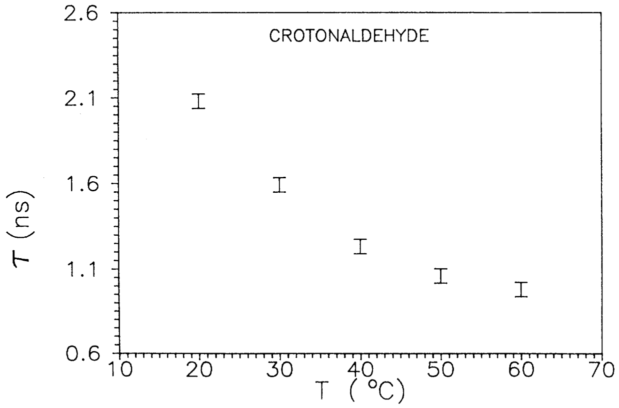

FIG. 3. Temperature dependence of chemical relaxation time of crotonaldehyde.

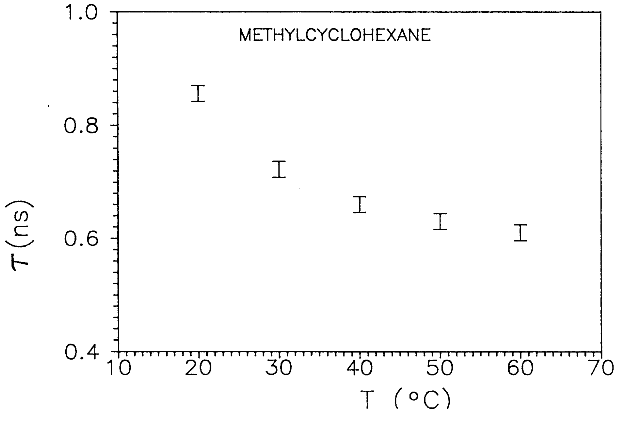

FIG. 4. Temperature dependence of chemical relaxation time of methylcyclohexane.

represent the temperature variation of the chemical-reaction time for both fluids. At each temperature, the thermal diffusivity D_T is given by the slope of the center-Rayleigh-line half-width as a function of q^2, according to the relation

$$\Gamma = D_T q^2 + 1/\tau ,$$

where τ is the relaxation time of the chemical reaction and Γ is the half width at half maximum.

The results for the thermal diffusivity are reported in Table I. We found that these experimental values are in good agreement with the values obtained with available temperature-dependent transport and thermodynamic coefficients.

The viscosity coefficients η decrease when the temperature increases in most of the simple liquids. In the temperature range 20–60 °C there is a small decrease as found in [6] and as predicted by the empirical viscosity laws [7].

The density-temperature dependence was found in the literature [6] and the values are reported in Table II.

For the methylcyclohexane, the thermal conductivity λ is described by the empirical Briggs law [5]:

$$\lambda = \lambda_{T_0}[1+\alpha(T-T_0)] ,$$

where α is a coefficient characteristic of each fluid. For methylcyclohexane, its value is $-0.08\ \mathrm{J\,cm^{-1}\,°C^{-2}}$ in the temperature range 30–70 °C.

For crotonaldehyde the temperature dependence of the thermal conductivity is available in literature [10] and also using the general formula of Scheffy and Johnson, who take into account the fusion point [7], we have

$$\lambda = 4.66\times 10^{-3}\frac{1-0.00126(T-T_M)}{T_M^{0.126}M^{0.3}} .$$

The temperature variation of the chemical-reaction characteristic time is obtained using different temperature plots like the ones given in Figs. 1 and 2. As stated in Ref. [1], the time measured at room temperature is in good agreement with the results obtained by ultrasonic measurements, essentially the ones deduced by Lamb [12]. The variation of $K(T)$ with temperature is reported in Table III.

The nonlinear behavior we found for the relaxation time, as can be seen in Figs. 3 and 4, suggest an analysis in terms of a Arrhenius law as fond in early ultrasound works like Ref. [12]. As can be seen in Figs. 5 and 6 there is reasonable agreement with an Arrhenius law and we can deduce the activation energy with good accuracy.

In fact, following a Lamb analysis, we use the expression

TABLE I. Thermal diffusivity values ($10^5\ \mathrm{cm^2\,s^{-1}}$) deduced from the slope of the plot central line versus the square of the wave vector q^2.

T (°C)	20	30	40	50	60
Methylcyclohexane	7.6	7.5	7.3	7.15	7.0
Crotonaldehyde	11.16	11.24	11.4	11.60	11.8

TABLE II. Temperature dependence of the density.

T (°C)	20	30	40	50	60
Methylcyclohexane	0.769	0.760	0.752	0.745	0.7400
Crotonaldehyde	0.870	0.845	0.810	0.775	0.745

TABLE III. Temperature dependence of the thermodynamic quantity $K(T)$. See text for more details.

T (°C)	20	30	40	50	60
Methylcyclohexane	0.011	0.010	0.009	0.008	0.007
Crotonaldehyde	0.010	0.085	0.068	0.058	0.051

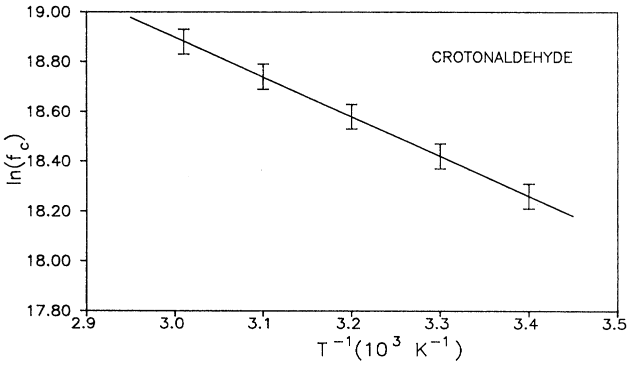

FIG. 5. Semilogarithmic plot of characteristic frequency of crotonaldehyde versus the inverse of the temperature.

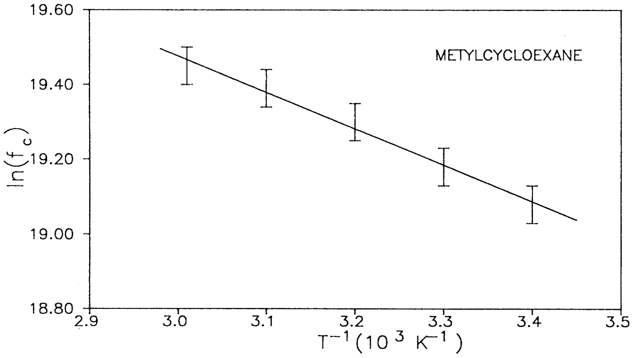

FIG. 6. Semilogarithmic plot of characteristic frequency of methylcyclohexane versus the inverse of the temperature.

TABLE IV. Activation enthalpy $\Delta H_2^{\ddagger}$ in $\mathrm{kcal\,mol^{-1}}$ and activation entropy $\Delta S_2^{\ddagger}$ in $\mathrm{cal\,mol^{-1}\,K^{-1}}$.

	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$
Methylcyclohexane	22	−222
Crotonaldehyde	43.92	−175

TABLE V. Values of $\rho^{-1}\eta_L$, the linear longitudinal kinematic viscosity (cP g^{-1} cm^3) and v, the sound velocity (m sec^{-1}) for the two studied fluids and for different temperatures.

T (°C)	20	30	40	50	60
	$\rho^{-1}\eta_L$; v	$\rho^{-1}\eta_L$; v	$\rho^{-1}\eta_L$; v	$\rho^{-1}\eta_L$; v	$\rho^{-1}\eta_L$; v
Methylcyclohexane	6.83; 1358	6.65; 1286	6.45; 1210	6.25; 1210	6.1; 1078
Crotonaldehyde	7.0; 1320	6.8; 1297	6.6; 1268	6.4; 1245	6.2; 1216

$$\ln\frac{f_c}{T}=-\frac{\Delta H_2^{+}}{RT}+\frac{\Delta S_2^{+}}{R}+\ln\frac{K_B}{2\pi h}\ ,$$

where f_c is the characteristic frequency related to the relaxation time by

$$f_c^{-1}=2\pi\tau\ ,$$

and the expressions

$$\tau=(h/F_2K_BT)\exp(\Delta H_2^{+}/RT)$$

and

$$F_2=\exp(\Delta S_2^{+}/R)\ ,$$

where h is the Planck constant.

We define ΔS_2^{+} and ΔH_2^{+} as entropy and enthalpy contribution to the activation energy of the characteristic time of the chemical reaction.

The temperature dependence of the characteristic frequency f_c allows to extract ΔS_2^{+} and ΔH_2^{+}. The values are reported in Table IV.

The dependence of the Brillouin position with temperature is monotonic with temperature and the velocity variation obtained with the fit of this mode, is given in Table V. The sound velocity decreases with temperature as usual in molecular liquids. We note that the Lebowitz [13] state equation for hard spheres describes correctly the sound peak position.

The sound absorption term, related to the width of the Brillouin line in the framework of the hydrodynamic theory, is almost independent of the thermal diffusivity coefficient, because the viscosity contributions dominate this linewidth. The values of the contribution of the viscosity terms are evaluated with some accuracy because the contribution $(\gamma-1)D_T$ is usually less than 1%. Values of viscosities are reported in Table V and we can note that decreases with temperature are obtained as expected, in agreement with usual behavior of molecular fluids.

In this work we found that the thermal variation of the experimentally detected transport and thermodynamic properties of the studied fluids follows the usual thermal dependence, and we were able to determine the evolution of the characteristic time of the chemical reaction detected previously. It was possible to describe this characteristic time with an Arrhenius law, in agreement with but with much more precision than the results obtained by ultrasonic measurements.

This work shows that the characteristic time of the chemical reaction is not only in good agreement with the values obtained at room temperature by ultrasonic measurements as shown in Ref. [1], but also its temperature variation can be described with an Arrhenius law. These results support the identification of this characteristic time with the chemical-reaction process.

ACKNOWLEDGMENTS

We acknowledge Dr. J. C. Lassègues for scientific discussion and his help in sample preparation and CCRRDT of Region Aquitaine for financial support. The Centre de Physique Moléculaire Optique et Hertzienne is associé au Centre National de la Recheche Scientifique URA No. 283.

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