Temperature Dependence of Collisional Energy Transfer in Ethyl Acetate

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Results are reported for the temperature and pressure dependence of the rate coefficient for the thermal unimolecular decomposition of ethyl acetate, obtained by using very low-pressure pyrolysis (VLPP) over the range 800-1150 K, both under conditions where only gas/wall collisions occur and also (at 837 K) dilute in a number of bath gases (He, Ar, Ne, Kr, N_2 , and C_2H_4). Solution of the appropriate reaction-diffusion master equation yields from these data both the extrapolated high-pressure rate coefficient $(10^{12.7} \exp(-201.5 \text{ kJ mol}^{-1}/RT))$ s^{-1}) and the average downward collisional energy transfer, $\langle \Delta E_{\rm down} \rangle$. The $\langle \Delta E_{\rm down} \rangle$ values are compared with those obtained for the same collision partners at ca. 340 K using multiple-photon dissociation (mpd). It is found that, for mon- and diatomic bath gases, $\langle \Delta E_{\text{down}} \rangle$ is approximately proportional to $T^{-(0.1-0.3)}$ (for He, Ne) and to $T^{-(0.3-0.5)}$ (for Ar, Kr, N₂). The combination of thermal and mpd techniques used here is generally applicable to obtaining collisional energy-transfer data of highly vibrationally excited molecules over a wide range of temperatures and collision partners.

Introduction

There is at present no generally accepted theory which enables one to calculate reliably the distribution function describing energy transfer in collisions between a bath gas molecule and a molecule with high internal energy (e.g., one which is undergoing unimolecular decomposition or termolecular recombination). Such a theory is desirable both for intrinsic interest and because, for example, it would be especially useful for the interpretation and prediction of rate data pertinent to aerochemical and combustion systems. Clearly, extensive data (viz., over a range of collision partners, temperatures, and internal energies) on such energy transfer are necessary both for establishing a phenomenological basis for the development of any theoretical description and for providing a quantitative test of its validity.

While extensive data for average energy transfer covering a wide range of collision partners at fixed temperatures are available,¹ there is a paucity of information on collisional energy transfer, for a given set of collision partners, with a sufficiently wide range of temperature or internal energy, although such data are gradually accumulating.²⁻⁴ However, a difficulty with methods used hitherto to obtain such results is that they are only applicable to special systems, for example, where reaction in the ground electronic state may be induced by singlephoton excitation to an excited electronic state which then undergoes rapid internal conversion to the ground state.^{2,3} In the present paper, we give, for the first time, collisional energy-transfer data over an extreme temperature range (ca. 340-850 K) obtained by a combination of two techniques which are quite widely applicable: multiple-photon decomposition (mpd) for low temperatures and pressure-

dependent thermal rate coefficients for high temperatures. These two techniques may be used on a wide range of reactants; however, it will be seen that meaningful results can only be obtained by using quite exacting combinations of experimental and theoretical techniques.

The particular system chosen for this first study is the decomposition of ethyl acetate:

$$CH_3CH_2OOCCH_3 \rightarrow C_2H_4 + CH_3COOH$$

Numerous conventional thermal studies have shown this reaction to be a clean unimolecular process free from side reactions and surface effects.⁵

Data for the ethyl acetate decomposition driven by multiple-photon activation have been given elsewhere.⁶ In these studies, the reactant was dilute in a number of bath gases. It was shown that values for the average downward collisional energy transfer can be obtained from fitting the pressure and fluence dependences of the fraction dissociated per pulse and of the average absorption cross section for the reactant dilute in bath gas; in the present work, the availability of more accurate RRKM parameters requires a refitting of these results. It is essential that this data fitting be via a numerical solution of the master equation which both is properly converged in energy grain size and takes temperature change into account (requirements which are computationally very demanding). We note at this point that some apparently anomalous energy-transfer results which have been obtained from similar mpd experiments⁷ may perhaps be in better accord with other systems if the data were reexamined in this light.

Data for the thermally induced decomposition of ethyl acetate are presented here. These were obtained by using the technique of pressure-dependent very low-pressure pyrolysis⁸ (VLPP). It has been previously established^{9,10}

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Figure 1. Experimental rate coefficients as function of temperature in VLPP reactor for different Z values (points). Line: RRKM fit using parameters of Table I and eq 3.

that this provides accurate energy-transfer data (as well as high-pressure rate parameters) provided that diffusive effects¹¹ and inefficient gas/wall collisional energy transfer⁹ are taken into account. Again, a computationally demanding solution of the resulting master equation is essential for data fitting.

Experimental Section

The VLPP experimental system and technique have been described elsewhere.^{8,12} The reactor used in the present study has aperture diameters of 1.07, 3.36 and 10.1 mm, giving Knudsen cell collision numbers⁸ Z of 21 460, 2177, and 260, respectively. The gas/wall collision frequency $\omega_{\rm w}$ is given by $(4.1 \times 10^3) (T/M)^{1/2} \, {\rm s}^{-1}$, where T is the temperature (K) and M the molecular weight of reactant (amu).

Ethyl acetate (Merck Darmstadt) and acetic acid (BDH) were thoroughly degassed and vacuum distilled bulb-tobulb before use. Tetrafluoromethane (Matheson, 99.7%) was used as an internal standard for the mass-spectrometric measurements. The inert bath gases for the pressure-dependent studies, helium (Matheson), neon (Matheson), argon (CIG), krypton (Matheson), nitrogen (J. T. Baker), and ethylene (Matheson), were all $\geq 99.5\%$.

Ethyl acetate decay was quantitatively monitored by the fragment peak at m/e 61, and acetic acid formation by its molecular peak at m/e 60 with CF₄ at m/e 69 as an internal standard.

Results

Thermal Dissociation. Rate coefficients were obtained both with undiluted reactant at pressures sufficiently low that only gas/wall collisions occur and with reactant dilute in various bath gases at pressures such that both gas/gas and gas/wall collisions are effective. Reactant:bath gas ratios (ca. 1:80) were such that reactant/reactant collisions can be safely neglected. The measured rate coefficients (average of ester decay and acid formation) are shown in Figures 1 and 2. The gas/wall collision-only rate coefficients (Figure 1) were found to be independent both of reactor collision number Z and of flow rate, as expected



Figure 2. Rate coefficients at 837 K with various bath gases as functions of pressure. Points: experiment. Lines: Theoretical fit from eq 1-3.

for this unimolecular process.

The rate data were then processed to obtain the required quantities (microscopic rate coefficients, collisional energy-transfer distribution function, and gas/wall collision efficiency) by solution of the appropriate master equation: 11

$$-Dr^{-2}[\partial(r^2G)/\partial r^2] - \omega \int [P(E,E') \ G(E',r) - P(E',E) \ G(E,r)] \ dE' + k(E)G(E,r) = RG(E,r)$$
(1)

where R is the rate coefficient, E the internal energy, k(E)the microscopic reaction rate, D the diffusion coefficient, ω the gas/gas collision frequency, P(E,E') the appropriately normalized⁹ distribution function ("probability") for collisional energy transfer from E' to E, r the radial variable, and G(E,r) the reactant population distribution. This equation must be solved with the appropriate boundary condition, viz.¹¹

$$-D(\partial G/\partial r)|_{r=r_0} + \frac{1}{3}\beta_{\rm w}\omega_{\rm w}[V^{-1}f(E) - G(E,r_0)] = 0 \quad (2)$$

where r_0 is the rector radius, V the reactor volume, $\beta_w(T)$ the temperature-dependent gas/wall collision efficiency, and f(E) the equilibrium distribution function, $f(E) = \rho(E)$ $\exp(-E/k_{\rm B}T)$, where $\rho(E)$ is the reactant density of states.

The method for the solution of eq 1 has been given previously.¹¹ The temperature dependence of β_w was chosen to be

$$\beta_{\rm w} = \min \left(1, a e^{-bT} \right) \tag{3}$$

min referring to the smaller value, and a and b being constants for a given reactant/wall system. This functional form has been shown to provide a good fit for $\beta_{w}(T)$ as determined from extensive sensitive multichannel data.¹⁰ The values of a and b were estimated from an empirical relation¹³ which is generally able to predict β_w to the ac-

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TABLE I: RRKM Parameters for Ethyl Acetate

Frequencies/cm⁻¹ (degeneracies in parentheses)

- reactant: 3000 (8), 1740, 1450 (6), 1390, 1280, 1150 (5), 900 (3), 780 (3), 640, 400 (3), 147 (2), 100 plus one free internal rotation, B = 0.387 cm⁻¹, symmetry number = 3
 - complex: 3000 (7), 2200 (1), 1450 (5), 1400 (1), 1310 (2), 1140 (5), 850 (2), 710 (3), 575 (1), 400 (5), 200 (2), 229 (1)

critical energy $\dot{E}_0 = 191.2 \text{ kJ mol}^{-1}$

molecule and activated complex assigned the same external moments of inertia product and values of (external symmetry number)/(number of optical isomers)

hard-sphere collision diameters given in ref 6

curacy required for the interpretation of these VLPP experiments. P(E,E') was chosen to be an exponential-cube for downward energy transfer

$$P(E,E') = N(E') \exp[(E - E')^3 / \alpha^3] \qquad E < E' \quad (4)$$

where N(E') is a normalizing factor^{1,14} and α a parameter to be determined from the data fitting; P(E,E') for E >E' is then fixed by microscopic reversibility. The foregoing functional form has been shown to fit sensitive high-temperature multichannel data.¹⁰ The collision frequency ω was calculated from the hard-sphere expression, using hard-sphere parameters given elsewhere.⁶ k(E) was determined from RRKM theory in the usual way. First estimates of the RRKM frequencies and critical energy (E_0) were taken from those of Beadle et al.⁵ and the lowest few frequencies of the activated complex and E_0 were then least-squares fitted to the data for gas/wall collisions only. In this fitting, it was assumed that reactant and activated complex have the same (external) moments of inertia product. To test the sensitivity of our results to assumptions made concerning the RRKM parameters, values for k(E) were obtained both with the proper inclusion of the reactant free internal rotation (Table I) and with this degree of freedom "frozen out" and replaced by an equivalent vibrational frequency.⁶

The preferred set of parameters for the reactant molecule is that shown in Table I. These parameters (which include a free internal rotation), along with the value of the moment of inertia product suggested by Beadle et al.⁵ $(1.872 \times 10^{-113} \text{ g}^2 \text{ cm}^6)$, give good agreement with the available thermodynamic data. Thus, the predicted entropy at 298 K is 359 J mol⁻¹ K⁻¹ (compared with the experimental value¹⁴ of 363 J mol⁻¹ K⁻¹) and the predicted values of C_p° are 125 J mol⁻¹ K⁻¹ at 360 K and 150 J mol⁻¹ K⁻¹ at 450 K (compared with the experimental values¹⁵ of 126 and and 150 J mol⁻¹ K⁻¹, respectively).

Having obtained $\rho(E)$ and k(E) as just described, we then obtained the appropriate energy-transfer parameter, $\langle \Delta E_{\text{down}} \rangle$ (see below), for each bath gas by fitting to the pressure-dependent results as given in Figure 2.

Before considering the final results of the data fitting, we examine the effects of the various foregoing asssumptions on the parameters so obtained. These effects can be simply estimated by changing the parameters involved within physically reasonably limits (e.g., changing *a* and *b* so that the value of β_w at the highest temperature considered changes by 0.1). Because we are studying a reaction with only a single decomposition channel (as distinct from the considerably more sensitive VLPP data from multichannel reactions,^{9,10}), the only meaningful measure of P(E,E) that we may obtain from our results is its first downward moment, the average downward collisional energy transfer $\langle \Delta E_{\rm down} \rangle$

$$\langle \Delta E_{\text{down}} \rangle = \frac{\int_{E < E'} (E' - E) P(E, E') dE}{\int_{E < E'} P(E, E') dE}$$
(5)

or equivalent quantities¹⁶ such as the collisional efficiency, β_c , the overall (upward plus downward) energy transfer, $\langle \Delta E \rangle$, or the root-mean-square overall energy transfer, $\langle \Delta E^2 \rangle^{1/2}$; one notes however that it is $\langle \Delta E_{\rm down} \rangle$ which is the optimal parameter to express energy-transfer data such as those given here.¹⁷ Changing the functional form of P(E,E') from that given in eq 4, while maintaining the same value of $\langle E_{\rm down} \rangle$, gives computed rate coefficients (at least over the pressure range involved in the present experiments) which are experimentally indistinguishable. Changing the values of a and b in eq 3 over a physically reasonable range changes the fitted value of $\langle \Delta E_{\rm down} \rangle$ by ca. $\pm 20\%$ at most. Changing the RRKM model as above, by incorporating free internal rotation as opposed to a torsion, changes $\langle \Delta E_{\rm down} \rangle$ by ca. $\pm 10\%$.

A useful measure of the sensitivity of pressure-dependent data to $\langle E_{\rm down} \rangle$ and to high-pressure parameters is afforded by the quantities R/R_{∞} and $R_0\omega/R$, where R_{∞} is the high-pressure-limit rate coefficient and R_0 the (dimensionless) low-pressure-limit rate coefficient. For the present system, with N₂ and monatomic bath gases, $R/R_{\infty} \sim 0.3$, $R_0\omega/R \sim 10^{-2}$, showing that the data should be quite sensitive to both $\langle \Delta E_{\rm down} \rangle$ and high-pressure parameters. However, for C₂H₄ as bath gas, the rate coefficient is closer to the high-pressure limiting value at comparatively low pressures of bath gas, and so these results are less sensitive to $\langle \Delta E_{\rm down} \rangle$.

Other meaningful results from our data fitting are the extrapolated high-pressure Arrhenius parameters, A_{∞} and E_{∞} . We find $E_{\infty} = 201.5 \pm 4$ kJ mol⁻¹, log $(A_{\infty}/s^{-1}) = 12.7 \pm 0.2$ (at 1000 K) in good agreement with the results of other workers.⁵ In particular, the RRKM parameters of Table I give good agreement with the VLPP data of Beadle et al.,⁵ using the appropriate parameters for β_{w} .

Fitted values of the rate coefficients are shown in Figures 1 and 2. $\langle \Delta E_{\rm down} \rangle$ values (as well as $\beta_{\rm c}$ values computed from the corresponding P(E,E')) are given in Table II. All RRKM calculations were carried out by using the computational procedures of Astholz et al.¹⁸ for the direct of count of densities of states involving free internal rotations.

Multiple-Photon-Dissociation Results. Extensive data on the multiple-photon dissociation of ethyl acetate, dilute in a number of bath gases, have been given by Eberhardt et al.⁶ These results consist inter alia of the fraction dissociated per pulse (f) and average absorption cross section $(\sigma_{\rm b})$ as functions of both fluence (F) and bath gas pressure (p). The reactant was sufficiently dilute in the bath gases (2 Pa of ethyl acetate in 100–600 Pa of bath gas) that reactant/reactant collisions can be safely ignored when interpreting the data, although it is important to note that even at these dilutions there is a significant temperature rise during the course of dissociation which must be taken into account in the analysis. In addition to the results of Eberhardt et al., multiple-photon-dissociation data for ethyl acetate have also been given by Danen et al.¹⁹ However, the studies of the latter workers employing

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TABLE II: Average Energy-Transfer Quantities for Ethyl Acetate/Bath Gas Collisions^a

bath gas	n	$\langle \Delta E_{\rm down} \rangle$, cm ⁻¹	$\langle \Delta E^2 \rangle^{1/2}, \mathrm{cm}^{-1}$	β _c	$-\langle \Delta E \rangle$, cm ⁻¹	
	***************************************	From Thermal I	Data at $T = 837$ K			
\mathbf{He}		300	354	0.02	50	
Ne		400	468	0.04	72	
Ar		550	635	0.07	131	
Kr		500	578	0.06	110	
Ν,		500	578	0.06	110	
$C_{2}H_{4}$		600 (?)	690 (?)	0.08 (?)	155 (?)	
		From mpd D	ata, T = 340 K			
He	$0.2(\pm 0.1)$	350	430	0.2	182	
Ne	$0.3(\pm 0.1)$	500	610	0.3	300	
Ar	$0.5(\pm 0.3)$	900	1150	0.5	670	
Kr	$0.5(\pm 0.3)$	800	1000	0.5	570	
N,	$0.4(\pm 0.3)$	700	870	0.4	480	
$C_{2}^{2}H_{4}$?	2000 (?)	2600 (?)	0.7 (?)	1700 (?)	

^a $\langle \Delta E^2 \rangle^{1/2}$ and $\langle \Delta E \rangle$ calculated at $E = E_0$. n = exponent in eq 12.

bath gas were not at sufficiently high dilutions so that reactant/reactant collisions can be ignored, and thus these results cannot be used to obtain accurate ethyl acetate/ bath gas $\langle \Delta E_{\rm down} \rangle$ values.

Eberhardt et al. interpreted their data by numerical solution of the appropriate master equation:

$$\frac{\partial g(E,t)}{\partial t} = \omega \int [P(E,E') g(E') - P(E',E) g(E)] dE' - k(E) g(E) - [L^{A}(E) + L^{S}(E)]g(E) + L^{A}(E-h\nu) g(E-h\nu) + L^{S}(E+h\nu) g(E+h\nu) (6)$$

Here g(E,t) is the population at time t and energy E, and $L^{A}(E,t)$ and $L^{S}(E,t)$ are the rates of absorption and stimulated emission. In a molecule such as ethyl acetate, with such a high density of states that eq 6 is safely applicable (Quack's case B^{20}) one has also

$$L^{\mathrm{S}}(E) \ \rho(E) = L^{\mathrm{A}}(E - h\nu) \ \rho(E - h\nu) \tag{7}$$

where ν is the laser frequency, and also

$$L^{A}(E,t) = \sigma(E) I(t) / h\nu$$
(8)

where $\sigma(E)$ is the cross section for single-photon absorption of a molecule with energy E and I(t) the laser intensity. Equation 6 is coupled with the equation for the temperature evolution of the system:

$$dT/dt = (\phi/C_v) \int dE \left[(E - \Delta H)k(E) g(E) + \omega \int (E' - E)P(E,E') g(E') dE' \right]$$
(9)

Note the correction of an error in eq 12 of ref 6. Here C_v is the constant-volume specific heat of the mixture of mole fraction ϕ of reactant and $1 - \phi$ of bath gas, g(E) has been normalized to unity at t = 0, and ΔH is the enthalpy change. It is found that, given $\rho(E)$ and k(E), consistent sets of $\sigma(E)$ and P(E,E') (the latter as $\langle \Delta E_{\text{down}} \rangle$, the functional form being otherwise unimportant) can be determined which reproduce all f(F,p) and $\sigma_b(F,p)$ data.

In comparing $\langle \Delta E_{\text{down}} \rangle$ values obtained by different techniques at different temperatures, it is obviously necessary to use the same k(E) and $\rho(E)$ in interpreting both sets of results. Now, the computations of Eberhardt et al. used $\rho(E)$ and k(E) from a less accurate set of RRKM parameters compared with those derived to fit the present set of thermal data; in particular, their RRKM parameters



Figure 3. Fitted and observed values for fractional decomposition per pulse for 2 Pa of ethyl acetate in various pressures of Ar bath gas, as function of fluence. Observed values from ref 6; fitted are those recalculated in the present paper.

do not reproduce the zero-pressure limit of the VLPP results with sufficient accuracy to be used to interpret the present pressure-dependent VLPP results. In addition, the fitting of Eberhardt et al. did not make allowance for the possibility of a temperature-dependent $\langle \Delta E_{\rm down} \rangle$. Finally, an error in the temperature-evolution equation of these authors (see eq 9) introduced an error of up to 10% in the derived $\langle \Delta E_{\rm down} \rangle$ values. For consistency in the present work, it was necessary to refit the data of ref 6 taking these various factors into account.

In refitting the mpd data, we employed the finite-difference method of Eberhardt et al., with the addition that it was found that computational speed and accuracy could be much improved by including an additional coupled differential equation, namely, that for df/dt:

$$df/dt = \int k(E) g(E) dE$$
 (10)

As pointed out by Eberhardt et al., it is essential in these computations to employ a sufficiently small grain size in the finite-difference equivalent of eq 6: energy grain sizes in excess of ca. $0.5\langle\Delta E_{\rm down}\rangle$ or $h\nu$ (whichever is the smaller) lead to gross inaccuracies in the computed value of the fractional decomposition. Note that eq 6 takes explicit account of collisions both during and after the laser pulse. A typical fit is shown in Figure 3.

In this refitting of the results of Eberhardt et al., the absorption cross section was assumed to take the empirical functional form

$$\sigma(E) = \sigma_0 \exp[-\zeta (E/h\nu)^\beta]$$
(11)

 σ_0 being the observed cross section for absorption at zero

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photons, and ζ and β being parameters to be determined. In the original fitting by Eberhardt et al., β was fixed at unity. However, it was found that, particularly with data covering the widest range of fluences, a quantitatively better fit could be obtained by allowing this parameter to vary. It was found in refitting that no unique set of values of the parameters $\langle \Delta E_{\text{down}} \rangle$, ζ , and β could be determined from the f(F,p) and $\sigma_{b}(F,p)$ data, for reactant dilute in bath gas, alone. However, these parameters can be determined uniquely by considering these data and the fluence dependence of f and $\sigma_{\rm b}$ for undiluted reactant at very low pressure (so that in the latter only postpulse collisions are important). In this way, it was found that $\zeta = 2 \times 10^{-5}$, $\beta = 3.5$ gave a good fit to the data. The $\langle \Delta E_{\text{down}} \rangle$ values resulting from the refitting are between 5% and 35% less than those obtained in ref 6. This change reflects both the correction arising from the error in the temperature-evolution equations in that work and the more accurate fitting in the present calculations, as well as taking account of the temperature dependence of $\langle \Delta E_{\rm down} \rangle$ in the present refitting. Note that the temperature rise is significant: e.g., a rise of 130 K after 3 μ s for 2 Pa of ethyl acetate in 200 Pa of Ne. The uncertainty in the present $\langle \Delta E_{\rm down} \rangle$ values is estimated as ca. 20%, obtained by varying the three fitted parameters to fit the data.

The refitted values of $\langle \Delta E_{\rm down} \rangle$, along with the corresponding values of $\langle \Delta E \rangle$ and $\beta_{\rm c}$, are given in Table II. Note that the results for ethylene as bath gas are subject to considerable uncertainty. This is because the computed solutions of the master equations with this bath gas show an enormous temperature rise, because of the low ethyl acetate/ethylene dilutions (typically 1:4, compared with 1:100 for other bath gases). In addition, for ethylene the total pressures were low (typically 50 Pa, compared with several hundred Pa for other bath gases); under such circumstances, it is likely that a nonadiabatic expansion takes place with C_2H_4 as bath gas, invalidating the assumptions made in deriving the master equation.

Also shown in Table II are the temperature exponents of $\langle \Delta E_{\text{down}} \rangle$, which was assumed for a given bath gas to have the functional form

$$\langle \Delta E_{\rm down} \rangle \propto T^{-n}$$
 (12)

with the value of the exponent *n* chosen to give the value of $\langle \Delta E_{\rm down} \rangle$ at 837 K to be that determined from the thermal experiments. The value of *n* for C₂H₄ bath gas is so uncertain that it is not given. For conciseness, all energy-transfer data from the mpd experiments are reported as results at T = 340 K, although of course the full temperature evolution during and after the pulse is taken into account in the fitting. The uncertainties in the values of *n* listed for other bath gases were calculated by assuming uncertainties of 10% and 20% for the values of $\langle \Delta E_{\rm down} \rangle$ at 837 and 340 K, respectively.

Discussion

The values of $\langle \Delta E_{\rm down} \rangle$ given in Table II for T = 340 and 837 K for ethyl acetate with collision partners He, Ne, Ar, Kr, and N₂ are quite consistent with those for similar systems.¹ The result for C₂H₄ as collision partner at T =837 K is significantly less than those values found with similar systems; we feel that our results for this collision partner are however unreliable, for reasons discussed above. Apart from the actual values of $\langle \Delta E_{\rm down} \rangle$, it is interesting to compare the variation of this quantity with collision partner with the variation observed with other systems. Our ethyl acetate/bath gas $\langle \Delta E_{\rm down} \rangle$ values (at both temperatures) vary as He < Ne < Kr ~ N₂ < Ar. Precisely the same order has been reported for azulene/ bath gas $\langle \Delta E_{\rm down} \rangle$ values by Barker and co-workers.²

It should be noted at this point that our $\langle \Delta E_{\rm down} \rangle$ values were obtained by assuming that this quantity is independent of the internal energy E, whereas Barker and co-workers² have shown that $\langle \Delta E_{\rm down} \rangle$ is in fact energy dependent. Fortunately, in the present case both thermal and mpd data are sensitive to approximately the same range of E: examination of the range of energies over which $g(E) \ k(E)$ and $G(E,r) \ k(E)$ are significant gives $2 \times$ $10^4 < E < 3 \times 10^4$ (where E is in cm⁻¹) for the mpd data and $1.8 \times 10^4 < E < 2.5 \times 10^4$ for the thermal results. Our $\langle \Delta E_{\rm down} \rangle$ values are thus averages over the actual E-dependent values of this range.

Our results show clearly that $\langle \Delta E_{\rm down} \rangle$ is a decreasing function of temperature, although for the lighter bath gases this temperature dependence is very weak. Thus, for He and Ne collision partners, the exponent *n* in eq 12 is 0.1–0.3, while for Ar, Kr, and N₂ it is ca. 0.4–0.5 (although the uncertainties in the *n* values for these sets of bath gases overlap, the trend is quite clear). The present energytransfer data cover a wider temperature range (a factor of 2.5 in absolute temperature) than ranges reported from any other study at the present time.

Our results may be compared to those of other workers on different systems. Studies by Rabinovitch and coworkers^{4,21} on isotopically substituted cyclopropanes show that, over the range 823–973 K, $\langle \Delta E_{\rm down} \rangle$ is approximately proportional to $T^{-1.5}$. This result can be rationalized in terms of a simple statistical model.²² On the other hand, Troe et al.³ report from their data on cycloheptatriene over the range 300-700 K that, for example, with Ar as collision partner, the overall energy transfer, $\langle \Delta E \rangle$, is independent of T over this range of temperature. Now, at low temperatures, the downward and overall energy-transfer values $\langle \Delta E_{\text{down}} \rangle$ and $-\langle \Delta E \rangle$, respectively) are very approximately equal, while $\langle \Delta E_{\text{down}} \rangle > |\langle \Delta E \rangle|$ at higher temperatures. While one would not expect quantitative transferability between collision partners as diverse as ethyl acetate and cycloheptatriene, the results of Troe et al. would seem to be qualitatively at variance with those found in the present work and in ref 4 and 21, since they imply that $\langle \Delta E_{\text{down}} \rangle$ increases with temperature. However, it should be pointed out that the solution of the master equation used in ref 3 to interpret the results did not have an exactly normalized form for P(E,E'), which can lead to inaccuracies in energy-transfer values at higher temperatures for molecules as large as cycloheptatriene.¹⁶ The results of ref 3 may thus need revision at higher temperatures.

For reasons that have been presented elsewhere,¹⁷ it is most meaningful to make comparisons of temperature dependences of energy-transfer quantities in terms of $\langle \Delta E_{\text{down}} \rangle$ rather than the collision efficiency or the overall energy transfer. However, one notes from Table II that these derived quantities also show a decrease with increasing temperature.

A number of qualitative explanation for the observed decrease in $\langle \Delta E_{\rm down} \rangle$ can be readily found. For example, it is predicted from simple statistical theories²² or, even more simply, by assuming that the downward or mean-square energy transfer will be a monotonic function of the duration of a collision. As pointed out by Barker and co-workers,² at the present time there are insufficient accurate data for energy transfer of highly excited molecules

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⁽²²⁾ See, for example: Oref, I.; Rabinovitch, B. S. Chem. Phys. 1977, 26, 385.

to be able to make a meaningful comparison with various theoretical models, which contain parameters that are difficult to evaluate a priori. The present work shows that the combination of laser mpd and thermal pressure-dependent VLPP offers considerable scope for obtaining further sensitive data for such comparisons, over a wide range of temperature, reactants, and collision partners.

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Registry No. He, 7440-59-7; Ar, 7440-37-1; Ne, 7440-01-9; Kr, 7439-90-9; N₂, 7727-37-9; C₂H₄, 74-85-1; ethyl acetate, 141-78-6.

Nitrogen-14 Nuclear Quadrupole Coupling Constants Effective for Nuclear Relaxation in Molecules of Trimethylalkylammonium Type

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The nitrogen nuclear quadrupole coupling constant $e^2 q Q/h$ in $(CH_3)_3 N^+ CH_2 X$ ions in aqueous solutions are obtained by the analysis of longitudinal nuclear relaxation times of ${}^{14}N$ and ${}^{13}C$ under the assumption that the motions effective for these two relaxation times $T_1({}^{14}N)$ and $T_1({}^{13}C_\beta)$ are the same. The experimental basis for the validity of this assumption is given. Within the experimental accuracy, the data consistently show the invariance of $e^2 q Q/h$ throughout the applied pH and temperature. The values of $e^2 q Q/h$ are 1 order of magnitude small compared with those of ordinary compounds (several MHz), as expected, and vary with X: 64 kHz for X = CH₂OH, 128 kHz for CH₂OCOCH₃, 190 kHz for COO⁻, and $\gtrsim 460$ kHz for COOH. The contribution from external field fluctuation due to water dipoles to the ${}^{14}N$ relaxation is negligible except for choline, which has the smallest value of $e^2 q Q/h$. The ${}^{14}N$ relaxation time of ammonium ions of this type is thus shown to be adequate for the study of molecular dynamics.

Introduction

The dominant mechanism of nuclear relaxation of the ¹⁴N nucleus in molecules in rapid motion is known to be the quadrupole interaction. The ¹⁴N relaxation method is a convenient tool for the study of molecular dynamics in liquids when the values of $e^2 q Q/h$ and η , the nuclear quadrupole coupling constant and its anisotropy parameter, are known.¹ These quantities are usually obtained by microwave spectroscopy, nuclear quadrupole resonance,² and NMR quadrupole splittings in solids or in liquid crystals.³ We have studied the dynamics of the $(CH_3)_3N^+CH_2$ group of phosphatidylcholine in single bilayer vesicles by ¹⁴N NMR,⁴ where the analysis has been done with $e^2 q Q/h$ evaluated for a related compound.⁵ It is because $e^2 q Q/h$ of $(CH_3)_3 N^+ CH_2 X$ ions are few and that of the lipid has not been available. Due to the nearly tetrahedral symmetry around the N nucleus, the electric field gradient at the nucleus should be small. Actually, the reported data of $e^2 q Q/h$ are in the vicinity of 100 kHz, which is 1 order of magnitude smaller than those of ordinary compounds of several MHz.3 The method of NQR is not applicable for the determination of $e^2 q Q/h$ of such low frequency. The $e^2 q Q/h$ in such molecules has been determined only by NMR. One method is to analyze ¹⁴N relaxation time, by using the reorientational correlation

time τ_c obtained by the other method. This is a useful method if τ_c is obtained as close as that effective for ¹⁴N relaxation. It is advantageous that η can be neglected in the analysis since the threefold symmetry around N should hold in the solution. Behr and Lehn⁶ obtained the coupling constant for acetylcholine bromide to be 140 kHz in D₂O and 120 kHz in CD₃OD with ¹⁴N and ¹³C relaxation times. Recently, measurements of ¹⁴N quadrupole splittings $\Delta \nu_Q$ in liquid crystals have been made.^{7,8} If the order parameter S is obtained independently, $e^2 q Q/h$ can be determined by the relation $\Delta \nu_{\rm Q} = (3/4)(e^2 q Q/h)S$. Siminovitch et al.⁷ determined the coupling constant to be 135 kHz from the $\Delta \nu_{Q}(^{14}N)$ of dipalmitoylphosphatidylcholine (DPPC) in multilamellar dispersions at 44 °C using $S_{C_{g-N}}$ calculated from the deuteron NMR quadrupole splitting of CD₃- $(CH_3)_2N^+$ in DPPC.⁹ The value is in good agreement with the result of Behr and Lehn.⁶ However, the temperature dependences of the quadrupole splitting⁷ and of the $S_{\mathrm{C}_{\mathrm{e}^{-}\mathrm{N}}}$ are different. This may be due either to the presence of temperature dependence of $e^2 q Q/h$ in the liquid crystal or to the inadequacy of the method of $S_{C_{\sigma}-N}$ evaluation. Measurements of the quadrupole splitting of the NMR spectra in the solid can also be used to determine $e^2 q Q/h$ and η in these nearly tetrahedral ¹⁴N compounds. In spite of the intermolecular contribution to $e^2 q Q/h$ and η due to

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