Table I. Arrhenius parameters for various reactions involving i-PrO.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log A ) (in sec(^{-1}) or (M^{\cdot+1}) sec(^{-1}))</th>
<th>( E ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CH(_4)+CH(_3)CHO (\rightarrow) i-PrO</td>
<td>8.3</td>
<td>11.5</td>
</tr>
<tr>
<td>(b) i-PrO (\rightarrow) CH(_3)(_2)COH</td>
<td>13.5</td>
<td>17.2</td>
</tr>
<tr>
<td>(c) i-PrO (\rightarrow) H(_2)CHCOCH(_3)</td>
<td>13.5</td>
<td>23.5</td>
</tr>
<tr>
<td>(d) H(_2)CHCOCH(_3) (\rightarrow) i-PrO</td>
<td>10.8</td>
<td>7.5</td>
</tr>
</tbody>
</table>

* Reference 6.

Aging (c) has a normal pre-exponential factor for a bond-breaking process of \(\sim10^{13.8}\) sec\(^{-1}\) and with \(E_a\) at 23 kcal/mole, \(d(\text{acetone})/dt = 70\times10^{-18}\) moles/ml-sec in excellent agreement with the observed 57.5\times10^{-13}\) mole/ml-sec.\(^4\) On this basis \(E_a = 7.5\) kcal/mole and \(A[\Delta S = 22.6 \text{ eu (1 atm)}^{1.8}] = 10^{10.5 M^{-1}} \text{sec}^{-1}\). This means that the reverse displacement process will be a very efficient process and probably accounts for the formation of CH\(_2\)O in the similar system of Linnett et al.\(^5\)

A general expression for acetone production is given by

\[ d(\text{acetone})/dt = k_b(k_b/k_a)^{1/2}(\text{CH}_3\text{CHO})^{3/2}K_{\text{a,b}}. \]

Using the data in Ref. 4, a graph is plotted of (CH\(_3\)CHO)\(^{3/2}\) versus \(d(\text{acetone})/dt\) (Fig. 1). An excellent straight line is produced which passes through the origin indicating that the displacement process is the only route to aceto ketone. Also, it supports the concept of i-PrO as an intermediate rather than a concerted reaction. i-PrO will be produced vibrationally excited but under the experimental conditions (10-200 mm) will be rapidly thermally equilibrated. From the slope of the graph we find \(k_b = 10^{2.84}\) sec\(^{-1}\), and hence, \(E_a = 23.5\) kcal/mole. Under the experimental conditions of Phillips et al.,\(^6\) Process (c) is at best 70 times slower than (b) (except possibly at low pressures since \(k_b\) might decrease much faster than \(k_a\) and is therefore unimportant, but there is a chance that CH\(_2\)CHCOH\(_3\) and, more important, H\(_2\) produced this way, would be observed at the highest temperature employed (200\(^\circ\)). Apart from very nicely explaining the formation of acetone in the pyrolysis of acetaldehyde, this note serves to emphasize the importance of these displacement processes in gas-phase reactions. The various estimated Arrhenius parameters are shown in Table I.

The author is indebted to Professor K. J. Laidler for his very clear suggestions.


Light Scattering as a Probe of Fast Reaction Kinetics

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(Rceived 16 June 1967)

The fine structure of the Rayleigh scattered light from a chemically reaction system offers, in principle, a novel method of following the reaction rate of even fast reactions without undue perturbation of the reacting system. The fine structure consists of two components: (1) a central one due to entropy fluctuations at constant pressure and (2) the Brillouin doublets due to pressure fluctuations at constant entropy which propagate at the velocity of sound of the reacting mixture, \(\mu_\text{react} (\omega)\) (in general a function of the frequency \(\omega\)). We focus primarily on the central, undisplaced component. For pedagogical clarity we consider the simple case of a dilute, liquid solution composed of an inert solvent of large heat capacity and two solutes \(S_1\) and \(S_2\) which are in dynamic equilibrium at the temperature \(T\), viz., \(S_1 \leftrightarrow S_2\) with \(K = c_{\text{eq}}^2/c_{\text{eq}} = K_{1/2}/k_0\)

where \(c_{\text{eq}}^2\) is the very small equilibrium concentration of species \(S_i\) (\(i = 1, 2\)), \(K\) is the equilibrium constant, and the \(k_i's\) are the rate constants for the forward (i) and backward (b) reactions. We assume in the following analysis that the density fluctuations are not coupled to fluctuations of the internal degrees of freedom. Within a volume element, small in comparison with the macroscopic sample in the scattering cell but large compared with molecular dimensions (i.e., of length comparable to the wavelength of incident light), there will exist fluctuations in the dielectric constant,

\[ \delta \varepsilon = (\partial \varepsilon/\partial \varepsilon_0) \delta \varepsilon_0 + (\partial \varepsilon/\partial \varepsilon_2) \delta \varepsilon_2 = K^{-1}(\delta \varepsilon/\delta \varepsilon_0) \delta \varepsilon_0 \]

\[ \delta \varepsilon = [K \delta \varepsilon_0 + \delta \varepsilon_2] \]

due to local concentration fluctuations, \(\delta \varepsilon_i\), of Species \(S_i\). There are also temperature fluctuations \(\delta T\) but these are only negligibly coupled\(^2\) to the concentration fluctuations in a sufficiently dilute system (\(c_{\text{eq}}^2\) very small) since the thermal diffusion coefficients are then proportional to \(c_{\text{eq}}^2\) and the relative concentration fluct-
tations can be made large so that the concentration flux is due to ordinary diffusion.

If we assume, as is usually done, that only $\delta c_e$ gives rise to light scattering, i.e., $(\partial\delta c_e/\partial T)\phi \approx 0$, then the intensity of scattered light is proportional to

$$
\iint \exp(i\omega t + i\mathbf{k} \cdot \mathbf{r}) \langle \delta c_e(r, r', 0) \delta c_e(r', t) \rangle \, d\mathbf{r} \, dt
= K^{-2} \langle \partial \delta c_e/\partial t \rangle \delta y(-\mathbf{k}, 0) \delta y(\mathbf{k}, \omega),
$$

where $\delta y(\mathbf{k}, \omega)$ is the real part of the space-time Fourier transform of $\delta y(\mathbf{r}, t)$ and $\delta y(\mathbf{k}, 0)$ is the Fourier transform of the initial fluctuation.

It is assumed that the local microscopic fluctuations satisfy the macroscopic phenomenological equations:

$$
\frac{\partial \delta c_e}{\partial t} = D_e \nabla^2 \delta c_e - k_e \delta c_e + k_e \delta c_e - (D_e \pm D_e)/2. \tag{1}
$$

This does not lead to a simple Lorentzian form for $i(\mathbf{k}, \omega)$, but shows clearly the increase in breadth with increasing $\tau_e$. If we further specialize to a system where the $S$ are structurally similar isomers (e.g., keto-enol tautomerism, etc.) for which $D_e \approx D_e \approx D_e \approx D_e \approx D_e$ and $D_e \approx 0$ then Eq. (2) gives

$$
i(\mathbf{k}, \omega) \propto \frac{k_b(K+1) + k^2D}{[k_b(K+1) + k^2D]^2 + \omega^2} \delta y(-\mathbf{k}, 0) \delta y(\mathbf{k}, 0). \tag{3}
$$

This formula clearly shows that (a) if the reaction rate $k_b(K+1)$ is sufficiently large compared with $k^2D$ for all $k$, or (b) if the scattering angle is so chosen that $k^2D$ is small compared with $k_b(K+1)$ then the major part of the unshifted linewidth is the reaction rate. The unshifted components of the Rayleigh line will be broadened by chemical reactions and this broadening can be used to study fast reaction kinetics

$$
(10^8 \lesssim k_b + k^2 \lesssim 10^{10}).
$$

A variety of phase-locked laser light sources which have been quite useful in the study of the Rayleigh scattering from nonreactive mixtures and pure fluids will be most useful here.

The measurement of the fractional light intensity $dI$ per unit frequency interval $d\omega$ in the Brillouin doublet provides a direct method for measuring the velocity and attenuation of an ultrasonic wave in the reacting liquid mixture. As such it represents a high-frequency extension of the usual ultrasonic method for studying kinetics of fast reactions. These and related matters will be more fully developed in a forthcoming paper.

We would like to acknowledge receipt, just prior to submission of this letter, of a first draft of a manuscript by L. Blum and Z. Salsburg, entitled “Light Scattering from a Chemically Reactive Fluid.” Despite the difference in treatment, the principal conclusions are very similar to ours.

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Comparison of Electron-Diffraction Intensity Measurements*

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In the rotating-sector–microphotometer method of electron diffraction no attempt is usually made to put the scattered-intensity data on an absolute scale. In view of the number of effects which must be corrected for, there has always existed a certain amount of doubt as to just how well the shape of absolute scattered electron intensities can be measured using photographic recording. For instance, the experimental data must be corrected for imperfection in the rotating sector, nonlinear blackening of the photographic plates, and extraneous scattering from apertures and residual gases in the vacuum system.

Absolute values of the total electron scattering cross sections (elastic plus inelastic) for $N_2$ and $O_2$ at 37 keV over the angular range $5^\circ < \theta < 70$ mrad (0.5 $< s < 8$) have recently been measured. These measurements have been made using a scintillator with a photomultiplier tube and should range in accuracy from $\pm 10\%$ at 5 mrad to $6\%$ at 70 mrad. In Figs. 1 and 2 recent photographic measurements from this laboratory obtained with 40-kV electrons for $O_2$ and $N_2$ are com-

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