TABLE I. Arrhenius parameters for various reactions involving i-Pr$\dot{O}$.

Reaction	log A (A in sec^{-1} or $M^{-1}\cdot sec^{-1}$)	E (kcal/mole)
(a) $\dot{C}H_3+CH_3CHO\rightarrow i\text{-Pr}\dot{O}$	8.3	11.5
(b) $i\text{-Pr}\dot{O}\rightarrow \dot{C}H_3+CH_3CHO$	13.5	17.2[a]
(c) $i\text{-Pr}\dot{O}\rightarrow \dot{H}+CH_3COCH_3$	13.5	23.5
(d) $\dot{H}+CH_3COCH_3\rightarrow i-\text{Pr}\dot{O}$	10.8	7.5

[a] Reference 6.

ing (c) has a normal pre-exponential factor for a bond-breaking process of $\sim 10^{13.5}$ sec^{-1} and with E_c at 23 kcal/mole, $d(\text{acetone})/dt$ is 70×10^{-13} moles/ml·sec in excellent agreement with the observed 57.5×10^{-13} mole/ml·sec.[4] On this basis E_d is 7.5 kcal/mole and $A_d[\Delta S^{\circ}=22.6$ eu (1 atm)$^{5,8}]$ is $10^{10.8}M^{-1}\cdot sec^{-1}$. This means that the reverse displacement process will be a verv efficient process and probably accounts for the formation of CH_2O in the similar system of Linnett *et al.*[9]

A general expression for acetone production is given by

$$d(\text{acetone})/dt=k_c(k_3/k_4)^{1/2}(CH_3CHO)^{3/2}K_{a,b}.$$

Using the data in Ref. 4, a graph is plotted of $(CH_3CHO)^{3/2}$ 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 acetone. Also, it supports the concept of i-Pr$\dot{O}$ as an intermediate rather than a concerted reaction. i-Pr$\dot{O}$ 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_c is $10^{7.04}$ sec^{-1}, and hence, E_c is 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_d) and is therefore unimportant, but there is a chance that CH_3COCH_3 and, more important, H_2 produced this way, would be observed at the highest temperature employed (200°). 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 comments.

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Light Scattering as a Probe of Fast Reaction Kinetics

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The fine structure of the Rayleigh scattered light from a chemically reacting 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]: (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, $u_{\text{react}}(\omega)$ (in general a function of the frequency ω). 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., $S_1\rightleftarrows S_2$ with $K=c_2^0/c_1^0=k_f/k_b$ where c_i^0 is the very small equilibrium concentration of species S_i $(i=1,2)$, K is the equilibrium constant, and the k's are the rate constants for the forward (f) 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,

$$\delta\epsilon_c=(\partial\epsilon/\partial c_1)_0\delta c_1+(\partial\epsilon/\partial c_2)_0\delta c_2$$
$$=K^{-1}(\partial\epsilon/\partial c_1)_0\delta y,$$
$$\delta y=[K\delta c_1+\delta c_2]$$

due to local concentration fluctuations, δc_i, of Species S_i. There are also temperature fluctuations δT but these are only negligibly coupled[2] to the concentration fluctuations in a sufficiently dilute system (c_i^0 very small) since the thermal diffusion coefficients are then proportional to c_i^0 and the relative concentration fluctuations can be made large so that the concentration flux is due to ordinary diffusion.

If we assume, as is usually done, that only $\delta\epsilon_c$ gives rise to light scattering, i.e., $(\partial\epsilon/\partial T)_0\approx 0$, then the intensity of scattered light[1] $i(\mathbf{k}, \omega)$ is proportional to

$$\iint \exp(i\omega t+i\mathbf{k}\cdot\mathbf{r})\,\langle\delta\epsilon_c(\mathbf{r}+r', 0)\,\delta\epsilon_c(\mathbf{r}', t)\rangle\, d\mathbf{r}\, dt$$

$$=K^{-2}(\partial\epsilon/\partial c_1)_0{}^2\,\langle\delta y(-\mathbf{k}, 0)\,\delta\bar{y}(k, \omega)\rangle,$$

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

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

$$\partial\delta c_1/\partial t=D_1\nabla^2\delta c_1-k_f\delta c_1+k_b\delta c_2,$$

$$\partial\delta c_2/\partial t=D_2\nabla^2\delta c_2+k_f\delta c_1-k_b\delta c_2, \qquad (1)$$

where D_i is the diffusion coefficient of S_i, and where the thermal diffusion, and the cross-diffusion terms are omitted on account of the diluteness of the system. One finds from Eq. (1) that

$$\frac{\delta\bar{y}(k, \omega)}{\delta y(-k, 0)}=\mathrm{Re}\left[\frac{i\omega\delta y(k, 0)+(\gamma_++k^2D_+)\,\delta y(k, 0)-(\gamma_-+k^2D_-)\,\delta x(k, 0)}{-\omega^2+(\gamma_++2k^2D_+)\,i\omega+(\gamma_+D_+-\gamma_-D_-)\,k^2+(D_+{}^2-D_-{}^2)\,k^4}\right], \qquad (2)$$

where $\delta x(k, 0)$ is the space Fourier transform of $\delta x(r, 0)=K\delta c_1(\mathbf{r}, 0)-\delta c_2(\mathbf{r}, 0)$, $\gamma_\pm=k_f\pm k_b$, and $D_\pm=(D_1\pm D_2)/2$. This does not lead to a simple Lorenzian form for $i(\mathbf{k}, \omega)$, but shows clearly the increase in breadth with increasing $\gamma_\pm$. If we further specialize to a system where the S_i are structurally similar isomers (e.g., keto–enol tautomerism, etc.) for which $D_+\approx D_1\approx D_2\approx D$, and $D_-\approx 0$ then Eq. (2) gives

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

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

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

A variety of phase-locked laser light sources which have been quite useful in the study of the Rayliegh 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.[1] 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 kV over the angular range $5<\theta<70$ mrad $(0.5<s<8)$ have recently been measured.[1] These measurements have been made using a scintillator with a photomultiplier tube and should range in accuracy from ±10% at 5 mrad to 6% at 70 mrad. In Figs. 1 and 2 recent photographic measurements[2] from this laboratory obtained with 40-kV electrons for O_2 and N_2 are com-