Dispersive Kinetics: A Structural Approach to Nonexponential Processes in Disordered Media†

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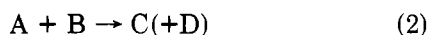*Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*

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Elementary chemical reactions of the form

$$A \rightarrow B + C \qquad (1)$$

and

$$A + B \rightarrow C(+D) \qquad (2)$$

are classified as unimolecular and bimolecular, respectively. Unimolecular reactions (1) follow first-order kinetics

$$d[A]/dt = -k_1[A] \qquad (3)$$

so that

$$[A]_t = [A]_0 \exp(-k_1 t) \qquad (4)$$

Bimolecular reactions (2) will appear to follow first-order kinetics if one of the reactants A or B is present in large excess, i.e.,

$$d[A]/dt = -k_2[A][B] \simeq -k_1^B[A] \qquad (5)$$

where $k_1^B = k_2[B]$ is essentially constant if $[B] \gg [A]$. All these reactions are characterized by an exponential decrease of the concentration of the limiting reactant and an exponential increase of one or more reaction products.

Occasionally one encounters reactions that appear to be elementary but do not follow the expected first-order kinetics. An example is hydrogen abstraction by alkyl radicals in organic glasses,

$$R^\bullet + HR' \rightarrow RH + {}^\bullet R' \qquad (6)$$
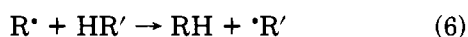
This reaction involves only a single step, hydrogen transfer from R′ to R, in an environment where the reactant HR′ is the solvent and thus present in large excess, so that eq 5 should apply. However, in glassy solvents, the kinetics is much better represented by an empirical relation of the form[1]

$$[R^\bullet]_t = [R^\bullet]_0 \exp[-(k_1 t)^\beta] \qquad 0 < \beta < 1 \qquad (7)$$

with β typically close to 0.5. This implies that the usual first-order rate constant, measured from $d \ln [R^\bullet]/dt$, is not constant at all, but decreases gradually during the course of the reaction. "Stretched" exponentials of the form 7 are not restricted to chemical reactions but have also been observed for physical relaxation pro-

cesses, such as mechanical[2] and dielectric[3] relaxation.

A variety of mechanisms have been proposed to explain such behavior.[4-11] Broadly speaking they fall into two classes. The first concerns reactions that are not truly elementary but require triggering by an inherently nonexponential process, e.g., diffusion. Thus in the example 6, one might think that hydrogen transfer requires a specific arrangement of solvent molecules near the sites of the radicals, brought about by thermal reorientation in the glass. Dependent on their initial configuration, some sites would rearrange more easily than others, which in principle can give rise to the behavior pattern of eq 7. Alternatively, one can demonstrate that even elementary reactions without outside triggering may exhibit such a pattern provided different sites react with different rates. Thus in the example of eq 6, one might assume that the hydrogen transfer rate depends on the shortest R–R′ distance, which varies from site to site in an inhomogeneous medium such as a glass. It has proved difficult, however, to find firm evidence for either of these mechanisms. Despite the many attempts to derive eq 7 theoretically,[4-11] it remains essentially an empirical relation and the physical significance of the parameters k_1 and β remains unclear. This has prevented the extraction of first-order rate constants and the evaluation of their dependence on temperature and other relevant parameters.

In our work we have followed a different approach. We did not try to work our way back to a physical model that leads to eq 7 since this has proved to be a tortuous path. Instead we began with simple structural and statistical arguments to derive a distribution of first-order rate constants and tried to relate the observed time dependence to this distribution.[1,12-14] Our approach is thus geared to deal with processes that do not require an external trigger. While its origins go back

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(1) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *Faraday Discuss. Chem. Soc.* 1984, 78, 175, and references therein.
(2) Kohlrausch, R. *Ann. Phys. (Leipzig)* 1847, 72, 393.
(3) Williams, G.; Watts, D. C. *Trans.Faraday Soc.* 1970, 66, 80. Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Trans. Faraday Soc.* 1971, 67, 1323.
(4) Zwanzig, R. *J. Chem. Phys.* 1965, 43, 714.
(5) Helfand, E. *J. Chem. Phys.* 1983, 78, 1931.
(6) Ngai, K. L. *Comments Solid State Phys.* 1979, 9, 127.
(7) Ngai, K. L. *Comments Solid State Phys.* 1980, 9, 141.
(8) Cohen, M. H.; Grest, G. S. *Phys. Rev. B* 1981, 24, 4091.
(9) Shlesinger, M. F.; Montroll, E. W. *Proc. Natl. Acad. Sci. U.S.A.* 1984, 81, 1280.
(10) Palmer, R. G.; Stein, D. L.; Abrahams, E.; Anderson, P. W. *Phys. Rev. Lett.* 1984, 53, 958.
(11) Rajagopal, A. K.; Teitler, S.; Ngai, K. L. *J. Phys. C: Solid State Phys.* 1984, 17, 6611.
(12) Doba, T.; Ingold, K. U.; Siebrand, W. *Chem. Phys. Lett.* 1983, 103, 339.
(13) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *J. Phys. Chem.* 1984, 88, 3165.
(14) Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *Chem. Phys. Lett.* 1985, 115, 51.

Table I.
Parameter Values Describing the Time Dependence of [CH$_3$·] in Methanol Glass

		eq 19			eq 7		
T/K	glass	$\bar{k}$/s^{-1}	γ	rms^a	τ^{-1}/s^{-1}	β	rms^a
87	CH$_3$OD	1.3×10^{-2}	1.5	0.228	2.2×10^{-2}	0.49	0.249
77	CH$_3$OH	4.4×10^{-3}	1.8	0.082	5.3×10^{-3}	0.49	0.130
77	CD$_3$OD	2.2×10^{-6}	3.0	0.358	1.6×10^{-6}	0.46	0.435
20	CH$_3$OH	7.9×10^{-5}	4.2	0.091	6.7×10^{-5}	0.33	0.113

^{a}Root-mean-square deviation from the best curve obtained by fitting the decay function to the raw data (as peak height against time) giving all points equal weight.

a long time,[15,16] it fell into disuse until recent investigations[1,14,17-22] showed that it can provide accurate fits to a variety of kinetic data sets. However, this by itself does not prove its validity. One way to check whether observed nonexponential behavior is due to a distribution of first-order processes, would be to probe the possibility of changing the time dependence by controlled manipulation of the distribution. Such a test has been performed for a reaction studied experimentally by Doba et al.[1,12-14] in our laboratory with results that confirm the validity of the concept. In the following sections we first review our analysis of this reaction and then suggest possible applications of the method to other processes in inhomogeneous media.

Methyl in Methanol: A Case Study

The example to be considered in this section is the decay of methyl radicals dispersed in a methanol glass.[1] The radicals abstract a hydrogen atom from the methyl group of a methanol molecule:

$$CH_3\cdot + CH_3OH \rightarrow CH_4 + \cdot CH_2OH \qquad (8)$$

The reaction is monitored by observation of the ESR signal of CH$_3$· and/or ·CH$_2$OH and is well-known to proceed nonexponentially in the glass. It was chosen for detailed study because kinetic data are readily obtained and because its simplicity makes it amenable to theoretical analysis.

The methyl radicals are generated in situ by one of a variety of photochemical processes, the final results being essentially independent of the source of the radicals. Special care was taken to standardize the conditions under which the glass was formed. The observed time dependence of the methyl radical concentration [CH$_3$·]$_t$ can be represented fairly accurately by the stretched exponential (7) as shown in Figure 1. The plotted [CH$_3$·]$_t$ are relative to [CH$_3$·]$_0$, the latter value being determined by the fit. Although we plot ln [CH$_3$·]$_t$, we have fitted eq 7 directly by Marquardt's modification of the Gauss–Newton–Raphson method, since the same error limits apply to all [CH$_3$·]$_t$ data points. Consequently, the (squared) deviations in Figure 1 do not fall equally above and below the straight lines. Had we fitted ln [CH$_3$·]$_t$ to t^β, we would have attached excessive significance to [CH$_3$·]$_t$ values measured at long times when the signal is weak.[21] The

(15) Wiechert, E. *Wied. Ann.* **1893**, *50*, 335, 546.
(16) Wagner, K. W. *Ann. Phys. (Leipzig)* **1913**, *40*, 817.
(17) Albery, W. J.; Bartlett, P. N.; Wilde, C. P.; Darwent, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1854.
(18) Jankowiak, R.; Richert, R.; Bässler, H. *J. Phys. Chem.* **1985**, *89*, 4569.
(19) Aubert, C.; Fünfschilling, J.; Zschokke-Gränacher, I.; Siebrand, W.; Wildman, T. A. *Chem. Phys. Lett.* **1985**, *122*, 465.
(20) Siebrand, W.; Somorjai, R. L.; Wildman, T. A. *FEBS Lett.* **1985**, *183*, 191.
(21) Siebrand, W.; Wildman, T. A. *Int. Rev. Phys. Chem.* **1986**, *5*, 251.
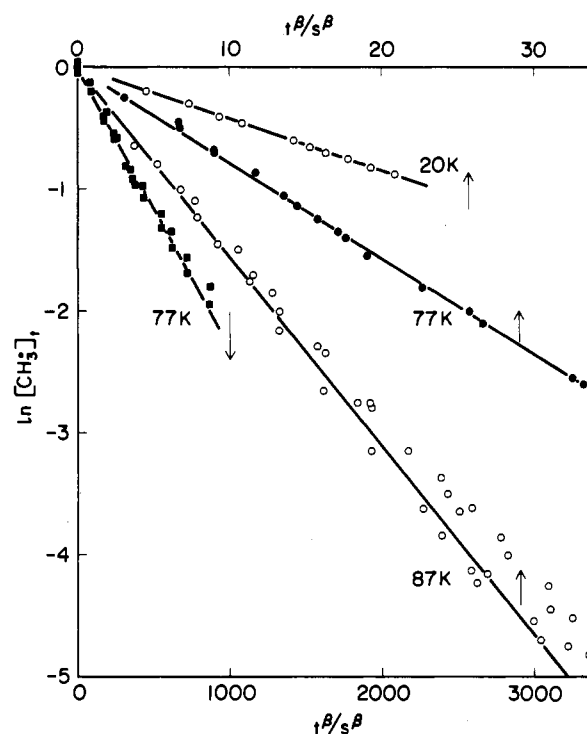(22) Richert, R.; Elschner, A.; Bässler, H. *Z. Phys. Chem.*, in press.

Figure 1. Time dependence of the methyl radical concentration in methanol glass. Circles (squares) refer to hydrogen (deuterium) transfer. Solid curves represent best fits of eq 7 to the experimental data. Parameter values are listed in Table I. Concentrations are relative to those at t = 0, which are taken from the fits.

present fit to the observed signal strength assigns equal weight to all data points. Parameter values are listed in Table I.

The transfer reaction is much slower in CD$_3$OD than in CH$_3$OH or CH$_3$OD (by three orders of magnitude at 77 K), indicating that nonclassical transfer, i.e., tunneling through a potential-energy barrier,[13] is the rate-determining step. This is confirmed by the observation that transfer persists at temperatures as low as 4 K, where it becomes nearly temperature-independent. If the reaction rate were determined by reorientation of the radical or the solvent, one would expect a small or zero isotope effect and a vanishing transition rate at low temperatures. Evidence for an effect of solvent reorientation, or diffusion of the radicals, has only been found near the glass transition temperature of 103 K. If this temperature is approached, the reaction shows quasi-first-order behavior, i.e., β approaches unity, presumably due to thermal averaging of the site structures. On the basis of this and other evidence,[1] we assume that for $T \lesssim 90$ K, hydrogen transfer is slow compared to intramolecular vibrations, optical lattice modes, and methyl rotations (including probably methyl radical tumbling), but fast compared

to diffusion of the radicals and reorientation of the methanol molecules in the glass.

Time-Evolution of the Rate Constant Distribution

The actual transfer probably involves a hydrogen from the (rotating) methyl group closest to the center of the methyl radical. Denoting the shortest distance between the carbon atoms of $CH_3^\bullet$ and CH_3OH by R_{min}, we assume that the R_{min} values show a distribution in the glass. If this assumption holds, the distribution will be time-dependent during the reaction and change towards higher R_{min} values, since the closest hydrogens transfer the fastest. This inference can be tested by variation of the illumination time τ, i.e., the time during which $CH_3^\bullet$ is generated, from values that are short to values that are long compared to $1/k_1$, defined by eq 7. For short τ, hydrogen transfer during the period τ can be neglected, but for long τ, some of the radicals generated will abstract a hydrogen during this period, namely those with small R_{min} values, leaving a distribution shifted towards larger R_{min} values. The resulting slowing down of the transfer with increasing τ is indeed observed.

This allows a quantitative test of the hypothesis that the nonexponential rate $f(t)$ is due to a distribution of exponential rate constants, $F(k)$, which in turn is due to a distribution of R_{min} values. Denoting the distribution of rate constants at the end of the illumination period τ by $F(k,\tau)$, we obtain the corresponding time dependence of $[CH_3^\bullet]$, $f(t,\tau)$, as the Laplace transform

$$f(t,\tau) = \int_0^\infty F(k,\tau) \exp(-kt)dk \qquad (9)$$

where

$$F(k,\tau) = N(k,\tau)/\int_0^\infty N(k,\tau)dk \qquad (10)$$

and $N(k,\tau)$ is the number of methyl radicals with a rate constant between k and $k + dk$ at time τ when the radical generation stops. We assume a constant photon flux during irradiation and a large excess of reactants so that their depletion is negligible. The generation of a specific subset of radicals characterized by a rate constant between k and $k + dk$ will thus be linear in time and the decay of this subset will be exponential:

$$dN(k,t)/dt = k_g c_0 G(k) - kN(k,t) \qquad (11)$$

where $k_g c_0$ is the overall rate of radical generation and $G(k)$ the fraction (normalized to unity) of radical precursors yielding radicals with rate constant k. Integration of (11) gives

$$N(k,\tau) = k_g c_0 G(k)[1 - \exp(-k\tau)]/k \qquad (12)$$

In the limit $\tau \to \infty$, the function $[1 - \exp(-k\tau)]/k$ varies much more slowly with k than does $G(k)$. If $G(k)$ peaks at k_0, we therefore obtain for long illumination times τ

$$F(k,\tau \to \infty) \simeq (k_0/k)F(k,0)[1 - \exp(-k\tau)] \qquad (13)$$

since $F(k,\tau) \to G(k)$ in the limit $\tau \to 0$.

This result allows us to estimate $F(k,\tau)$ if we know $F(k,0)$ or, equivalently, using (9), to estimate $f(t,\tau)$ if we know $f(t,0)$. Such a comparison is illustrated in Figure 2, where the broken line for $\tau = 1.4 \times 10^4$ s is derived from the solid line for $\tau = 10$ s, the latter being a model fit to eq 7. The good fit of the former curve to the data
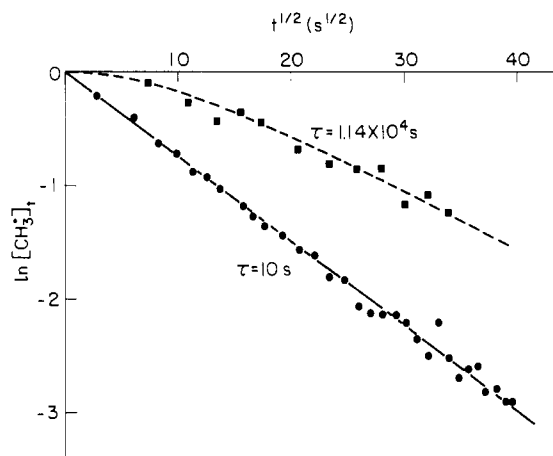
Figure 2. Time dependence of the methyl radical concentration in methanol glass at 77 K after brief and long illumination periods. The broken curve for $\tau = 1.4 \times 10^4$ s is derived from the distribution at $\tau = 10$ s, obtained by fitting to eq 7 (solid curve).

supports the concept of a distribution of exponential rate constants.

Other supporting evidence is obtained from the study of methyl in mixtures of CH_3OD and CD_3OD. In that case one expects a much broader distribution $F(k)$ than for pure isotopes. The observed time dependence $f(t)$ confirms this in that it yields a smaller value for the stretch parameter β than for the pure isotopes, namely 0.35 for $CH_3OD:CD_3OD = 1:9$ at 77 K against 0.49 for CH_3OH and 0.46 for CD_3OD.

For a quantitative interpretation of these observations we need a model to describe the distribution $F(k)$ in terms of the structure of the sites where the methyl radicals are trapped. We assume that each site corresponds to a characteristic transfer distance q, proportional to R_{min}. In the dilute solution, the sites will be independent since the transfer is a localized process. We assume that q will vary from site to site about an average $\bar{q}$ and that the $q - \bar{q}$ values will be small, random, and independent. In that case the q are expected to exhibit a Gaussian distribution

$$\Phi(q) = \pi^{-1/2}\Gamma^{-1} \exp[-(q - \bar{q})^2/\Gamma^2] \qquad (14)$$

Γ being the width parameter. To each site with a transfer distance between q and $q + dq$, we assign a rate constant between k and $k + dk$, so that $|\Phi(q)dq| = |F(k)dk|$. Explicit hydrogen transfer calculations indicate that for small $q - \bar{q}$, the rate constant k varies exponentially with distance
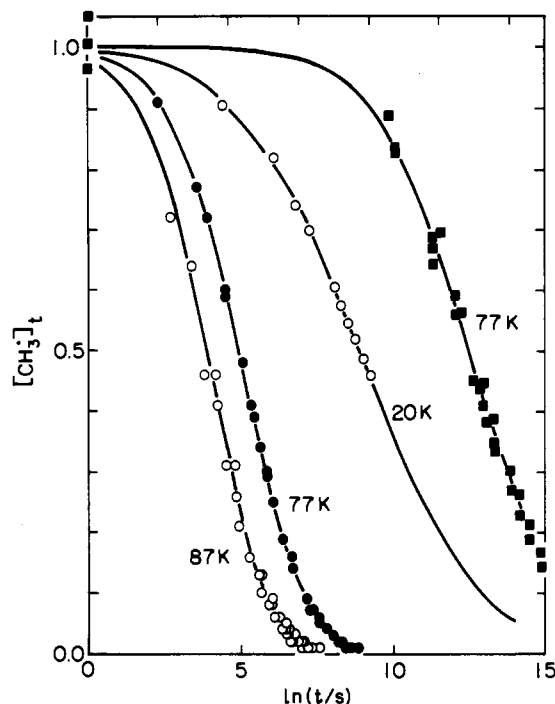
$$k = \bar{k} \exp[-\lambda(q - \bar{q})] \qquad (15)$$

Thus if $\Phi(q)$ is Gaussian, $F(k)$ will be a log normal distribution. Then we can rewrite the Laplace transform (9) as

$$f(t) = \int_\infty^0 \Phi(q) \exp[-k(q)t]dq =$$

$$\pi^{-1/2}\Gamma^{-1} \int_\infty^0 \exp[-(q - \bar{q})^2/\Gamma^2 - \bar{k}te^{-\lambda(q-\bar{q})}]dq$$

$$\approx \pi^{-1/2}\gamma^{-1} \int_{-\infty}^\infty \exp(-y^2/\gamma^2 - \bar{k}te^y)dy \qquad (16)$$

with the substitutions $y = \ln(k/\bar{k}) = -\lambda(q - \bar{q})$ and $\gamma = \lambda\Gamma$.

As shown in Figure 3, this equation provides an excellent fit to the kinetic data of methyl radicals in glassy

Figure 3. Time dependence of the methyl radical concentration in methanol glass. Circles (squares) refer to hydrogen (deuterium) transfer. Solid curves represent best fits of eq 16 to the experimental data. Parameter values are listed in Table I. Concentrations are relative to those at $t = 0$, which are taken from the fits. Points measured at t < 1 s are plotted as if measured at t = 1 s.

methanol. In Table I the statistical data of this fit are compard with those of the fit to eq 7 displayed in Figure 1. It follows that eq 16 provides a slightly better fit than eq 7, in addition to permitting a more meaningful physical interpretation.

In Figure 3 we have plotted $[CH_3^\bullet]_t$ against ln t rather than ln $[CH_3^\bullet]_t$ against t. In the present instance, the latter plot would not yield a straight line, but neither does the former. One reason for our choice of format becomes clear if we introduce a logarithmic time scale $z = \ln \bar{k}t$ into eq 16:

$$f(t) \simeq \pi^{-1/2}\gamma^{-1} \int_{-\infty}^{\infty} \exp[-y^2/\gamma^2 - \exp(z + y)]dy \quad (17)$$

Hence the plot of Figure 3 serves to separate the two parameters $\bar{k}$ and γ that govern the observed time evolution. The shape of $f(t)$ in Figure 3 is determined solely by the half-width of the Gaussian distribution of ln k values. Changing $\bar{k}$, the rate constant corresponding to the average transfer distance $\bar{q}$, only shifts the curve along the logarithmic time axis. Hence a plot of $[CH_3^\bullet]_t$ against ln t allows a convenient first estimate of γ and $\bar{k}$.[19]

An additional advantage of the format of Figure 3 compared to that of Figure 1 is that the quality of the fit can be judged visually, the error in the $[CH_3^\bullet]_t$ values being constant rather than proportional to the signal strength. To compare the fits displayed in the two figures, one should consult Table I where root-mean-square deviations are listed.

The parameter $\bar{k}$ allows us to associate a specific rate *constant* with the reaction, despite its nonexponential kinetics, and hence to study the dependence of the rate constant on temperature, etc., in the usual manner. The parameter γ contains information on the structure of

the inhomogeneous medium in which the reaction takes place; it provides a measure of structural disorder in the glass, scaled by the parameter λ which relates the rate constant to the transfer distance. If λ can be determined independently, e.g., by direct calculation, we can deduce how the transfer distance, and hence R_{min}, varies from site to site. Such calculations have been performed[1] and yield an average transfer distance of about 1.8 Å and a Gaussian half-width Γ of about 0.03 Å.

Hence in this instance, eq 16 has proved a powerful device for unraveling nonexponential kinetics. However, it has one drawback: the integration must be done numerically. Since the stretched exponential (7) also provides a reasonably accurate fit, one may ask whether an analysis based on this analytical equation can provide a useful alternative. Unfortunately, this is not the case. It is possible to obtain analytical expressions for the distributions $F(k)$ and $\Phi(q)$ associated with (7) from the inverse Laplace transform,[1,4] but the resulting distribution $\Phi(q)$, known in statistics as an extreme-value distribution, has no readily discernible physical significance in the case at hand. Hence conclusions based on such an analysis[23,24] should be treated with due caution.

The Structure of the Glass

We now return to the system of $CH_3^\bullet$ in a mixed CH_3OD–CD_3OD glass. Clearly, we can no longer associate the rate constant k at a given site with the shortest transfer distance (or with R_{min}), since it will matter a great deal whether this distance applies to H or D transfer. Therefore, we must consider the structure of the site in more detail and include all transfer distances for the first solvent shell. While the observed time dependence $f(t)$ can still be approximately explained by a Gaussian distribution of ln k values, the distribution of q values must be distinctly non-Gaussian since some of the k values are associated with hydrogen transfer ($\lambda = \lambda^H$) and others with deuterium transfer ($\lambda = \lambda^D > \lambda^H$).

If we assume that the local structure around $CH_3^\bullet$ in the glass resembles the structure of crystalline methanol with $CH_3^\bullet$ replacing CH_3OH, then $CH_3^\bullet$ will have six neighboring methyl groups, two at a distance R_1 and four at a distance $R_2 > R_1$.[25] If at least one of the R_1 methyls is CH_3, it is virtually certain that H will transfer; on the other hand, if none of the neighboring methyls is CH_3, transfer is limited to D. In all other cases there will be competition between H at R_2 and D at R_1, with both R_1 and R_2 showing distributions between sites. A detailed analysis of this system cannot yet be given since the available experimental data do not allow a unique fit to a full range of CH_3OD/CD_3OD mixtures. Preliminary results indicate that the number of nearest neighbors favored by the data is indeed six, as in the crystal. Under these conditions, $\Phi(q)$ is of course no longer Gaussian. The reason that a Gaussian works so well for an isotopically pure solvent must be that $\Phi(R_1)$ is approximately Gaussian and makes the dominant contribution except for very long times when the poor signal-to-noise ratio would prevent the de-

(23) Klochnikhin, V. L.; Trakhtenberg, L. I. *Zh. Fiz. Khim.* **1984**, *58*, 2877. [English translation: *Russ. J. Phys. Chem.* **1984**, *58*, 1747].

(24) Vyazovkin, V. L.; Bol'shakov, B. V.; Tolkatchev, V. A. *Chem. Phys.* **1985**, *95*, 93.

(25) Tauer, K. J.; Lipscomb, W. N. *Acta Crystallogr.* **1952**, *5*, 606.

tection of a $\Phi(R_2)$ contribution.

Although this analysis remains to be completed, it shows that, in principle, dispersive kinetics can be used to study structural properties of inhomogeneous systems. This approach appears to have great potential, since rate processes are often very sensitive to structural details.

Hole Burning

Since the principles underlying this approach to dispersive kinetics are quite general, we expect it to work for many other nonexponential processes, namely those for which the "reaction" is localized and the medium inhomogeneous. Evidence suggests that hole burning falls into this category.

An inhomogeneously broadened absorption band represents a distribution of narrower homogeneously broadened bands corresponding to molecules at different sites in an inhomogeneous medium. A monochromatic light beam will excite only molecules whose homogeneous band coincides with the laser frequency. If absorption is followed by a process other than emission, i.e., radiationless decay or photochemical reaction, the site may be permanently altered so that the absorption coefficient at this frequency will be permanently reduced, causing a dip ("hole") in the absorption band. Both the formation of the hole[18,19] and its subsequent isothermal decay[26] have been shown to proceed nonexponentially.

A typical example is the system of tetracene in a methyltetrahydrofuran (MTHF) glass. Excitation by a laser with a frequency in the region of the first absorption band of tetracene leads to fluorescence of tetracene molecules at the site corresponding to this frequency. Hole formation can be monitored through the gradual decrease of this fluorescence. Results based on data from two laboratories[19,22] are shown in Figure 4, together with the best fit to eq 16. This plot was first presented by Richert et al.[22] who demonstrated that eq 7 is less satisfactory in this case, showing substantial deviations for short times.

To interpret these results, we note that in the system at hand the hole is not the result of a photochemical reaction, the photon being too low in energy for such a process. It must therefore be due to a physical change at the site of the excited molecule. Since the measurements are carried out at very low temperatures ($T \lesssim 4$ K), it is not reasonable to assume diffusion of solute or solvent molecules. It seems much more likely that the excitation causes a local rearrangement of the site, possibly as a result of the charge redistribution caused by the excitation.[27] This might give rise to a potential-energy diagram of the type illustrated in Figure 5, which depicts potentials in the ground state (S_0) and excited state (S_1) of tetracene along a site coordinate such as the orientation of the tetracene molecule relative to surrounding solvent molecules. The potential minima on the left show no dispersion since they are selected by the laser frequency; those on the right describe the site after reorientation and will generally show dispersion since in the absence of long-range order no two sites will be completely identical. As depicted schematically in Figure 5, the corresponding distribu-

tion of displacements may also be thought of as a distribution of barrier heights. In the absence of tunneling, we can then replace eq 15 by the Arrhenius equation[17]

$$k = k_0 \exp(-E_a/k_B T) \qquad (18)$$

with k_B the Boltzmann constant. This approach redefines γ in eq 16 and 17 as $\gamma = \Gamma/k_B T$ and thus predicts the product γT to be independent of temperature. The available hole-burning data do not permit us to test this hypothesis, but they do conform to other predictions of the model.

Conclusions

Nonexponential rate processes are ubiquitous in chemistry and physics. In this contribution we have focused on one special group, namely rate processes that are basically exponential but whose rate constants vary from site to site in an inhomogeneous medium. This group, too, is probably widespread: quite a few candidates have been[1,17-20] or may be[26,28-30] identified in the literature. We have paid special attention to methods aimed at probing whether a particular nonexponential process belongs to this group. This problem is far from trivial since the obvious test of inverting the Laplace transform (9) is mathematically unstable in the sense that it cannot distinguish with sufficient accuracy between different distributions. Thus a given decay curve $f(t)$ may be reproducible within experimental accuracy by a continuous distributions $F(k)$, e.g., a Gaussian, or a discrete distribution.[31] To choose between these interpretations, we require additional information. In general, a continuous distribution can only be expected if there is structural disorder, as in glasses or polymers. Depending on the actual rate of the process being studied, the disorder in liquids may be structural or dynamic; the structural aspects are expected to dominate only for rate processes that are much faster than the motion of the molecules in the liquid. In crystals, one expects either discrete rate constants or collective effects.

Historically, the analysis leading to eq 16 was first applied[15,16] to the "wrong" processes, namely mechanical and dielectric relaxation, where collective effects are likely to be important. Recent efforts[4,6-11,32-35] to account for relaxation and transport processes in disordered systems have tended towards the opposite extreme: they appear to imply that processes proceeding roughly according to the stretched exponential (7) must involve collective effects or diffusion or both. The case of methyl in glassy methanol provides a powerful counter-example: experimental and theoretical evidence clearly indicates a noncollective and nondiffusive mechanism, leading to a rate law that is formally quite different from the stretched exponential. The fact that

(26) Breinl, W.; Friedrich, J.; Haarer, D. *Chem. Phys. Lett.* **1984**, *106*, 489; *J. Chem. Phys.* **1984**, *81*, 3915.

(27) Jankowiak, R.; Bässler, H.; Silbey, R. *Chem. Phys. Lett.*, in press.

(28) Plonka, A.; Kevan, L. *J. Chem. Phys.* **1985**, *82*, 4322.

(29) Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 6494.

(30) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579.

(31) See, for example: James, D. R.; Ware, W. R. *Chem. Phys. Lett.* **1985**, *120*, 450, 455. James, D. R.; Liu, Y.-S.; De Mayo, P.; Ware, W. R. *Chem. Phys. Lett.* **1985**, *120*, 460. Zimmermann, K.; Delaye, M.; Licinio, P. *J. Chem. Phys.* **1985**, *82*, 2228. James, D. R.; Ware, W. R. *Chem. Phys. Lett.* **1986**, *126*, 7.

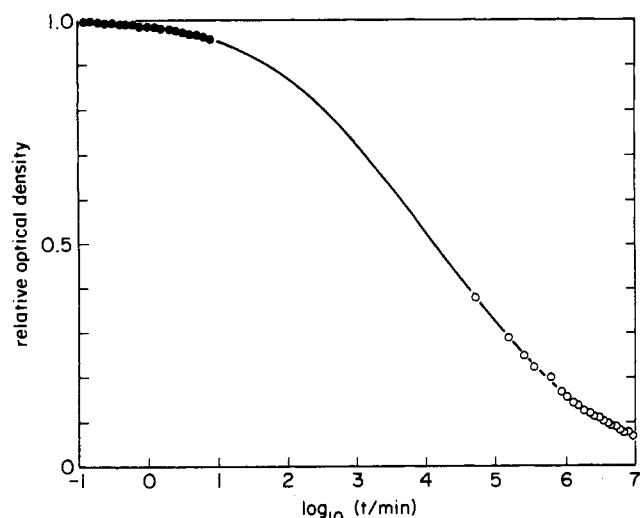(32) De Gennes, P.-G. *C.R. Acad. Sci. Ser. 2* **1983**, *296*, 881.

(33) Klymko, P. W.; Kopelman, R. *J. Phys. Chem.* **1983**, *87*, 4565.

(34) Klafter, J.; Blumen, A.; Zumofen, G. *J. Stat. Phys.* **1984**, *36*, 561.

(35) Anacker, L. W.; Kopelman, R.; Newhouse, J. S. *J. Stat. Phys.* **1984**, *36*, 591.

Figure 4. Hole burning in the inhomogeneously broadened absorption spectrum of tetracene in MTHF. The plot, adapted from Richert et al.,[22] is based on the short-time data points of ref 22 and the long-time points of ref 19. The solid line represents the "best" fit obtained with eq 16.
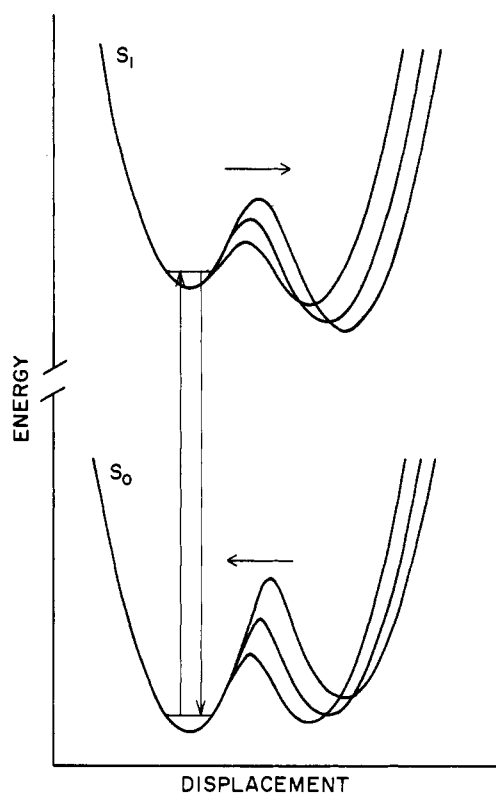
Figure 5. Schematic potential-energy diagram illustrating nonphotochemical hole burning. The abscissa refers to a coordinate describing reorientation of the absorbing molecule (tetracene) at a site in the inhomogeneous medium (glassy MTHF); it may be regarded as the reaction coordinate of hole burning (in the direction of the upper horizontal arrow on the excited-state (S₁) surface) and hole decay (lower arrow, ground-state surface). The minima at the left depict the original site selected by the laser and monitored by fluorescence. The series of minima at the right depict a distribution of final sites resulting from the absence of long-range order.

the data can also be fitted reasonably well with eq 7 cautions against a literal interpretation of such a fit: in the absence of data for very short and very long times, it may be a fluke. In practice, this means that fits to either eq 7 or eq 16 are significant only if supported by

an acceptable physical model. On this basis we expect the dispersive kinetics of eq 16 rather than the stretched exponential (7) to be appropriate for dilute solid solutions and low temperatures. The results for spectral hole burning seem to bear this out.

If the observed time dependence can indeed be assigned to dispersive first-order kinetics in a disordered medium, the analysis can proceed in several directions. The distributions $F(k)$ and $\Phi(\ln k)$ can be determined, the latter being amenable to physical interpretation in the form $\Phi(E_a)$ or $\Phi(q)$, where E_a and q are the energetic and structural parameters governing the rate process. From the mean values of E_a or q in their distributions Φ, one can derive a "most probable" rate constant $\bar{k}$ which characterizes the process as a first-order rate constant associated with the dominant site in the medium. This rate constant can be studied in the normal way as if the process were exponential.

The dispersion of k provides a measure for the disorder of the medium. In principle, this can be exploited in two ways, namely to investigate the local structure of the medium and to evaluate the dependence of the rate process on energetic or structural parameters. Our study of methyl in methanol illustrates both of these aspects. The dispersive kinetics makes it possible to relate the hydrogen transfer rate to the transfer distance, which relationship is amenable to theoretical evaluation. Together with transfer data measured in isotopically mixed methanol glasses, this opens the possibility of probing the arrangement of methanol molecules around the trapped radical.

In the case of hole burning the structural information needed for a detailed interpretation is not yet available. However, successful identification of the degrees of freedom responsible for the formation of a spectral hole may be within reach. Of particular interest is the possibility of applying the analysis to biological systems. As an example, we cite the time evolution of the recombination of the heme with O_2 or CO in heme proteins. Austin et al.[36] have shown that this recombination is geminate if the heme-ligand complex is photodissociated below 180 K. Under these conditions the ligand cannot escape from the heme pocket so that the recombination reaction is a localized, i.e., nondiffusive, process. In principle it should therefore be possible to explain the observed nonexponential rates for this process in structural terms,[20,37] leading to new insight in the interplay between biologically active molecules and the proteins in which they are embedded.

For the time being, such a detailed analysis will be possible only in exceptional cases. However, even in the case of systems for which no structural information is available, the approach remains useful since it extends the range of systems for which the kinetics can be analyzed.

(36) Austin, R. H.; Beeson, K. W.; Eisenstein, L.; Frauenfelder, H.; Gunsalus, I. C. *Biochem.* **1975**, *14*, 5355.

(37) Agmon, N.; Hopfield, J. J. *J. Chem. Phys.* **1983**, *79*, 2042.