Stimulation of chemical reactions by temperature microfluctuations in a medium absorbing laser radiation

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In those cases when a medium is heated by excitation and the molecules that absorb radiation resonantly are subsequently deactivated, microscopic temperature fluctuations are produced in the medium as a result of strong heating of small regions around the deactivated molecules. Notwithstanding the small volume and short lifetime of these regions, it is they which decide the rates of the chemical reactions when the medium is heated by UV radiation of sufficient intensity.

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INTRODUCTION

The temperature T of a medium that absorbs laser radiation depends on the time t and on the spacial coordinates $\mathbf{r}$, particularly because the laser pulse is of limited duration and irradiates a limited volume. This dependence frequently influences substantially the chemical reactions that take place in the medium as it is heated (see, e.g., Ref. 1). The present paper deals with a dependence of another type, microscopic, when the temperature T changes substantially within a time of the order of 10^{-11} sec and over a distance of the order of 10^{-7} cm. We shall show that if the medium is heated because it contains resonant molecules (or atoms), temperature microfluctuations of the type indicated must occur in it; they occur also when the laser operates in a certain sense in a cw regime and irradiates a large volume. We shall show that when the medium is heated by sufficiently powerful ultraviolet (UV) radiation the temperature microfluctuations increase the rates of chemical reactions with activation energy exceeding 10 kcal/mol, i.e., of practically all reactions; this increase is larger the higher the activation energy of the reaction.

The action of low-power UV radiation reduces as a rule to photochemical sensitization, meaning chemical reactions with participation of resonant molecules or with participation of other molecules to which a quantum $\hbar\omega_l$ can be transfered by collision,[2] where ω_l is the radiation frequency. Processes that proceed without the indicated molecules do not respond to low-power UV radiation, since this radiation hardly changes the average temperature of the medium. In view of the progress made in UV laser technology, it is of interest to investigated the purely thermal action of sufficiently strong UV radiation that influences all the temperature-dependent processes. It will be shown that this action does not reduce to a thermodynamic-equilibrium heating of the medium.

MICROSCOPIC PICTURE OF HEATING OF THE MEDIUM BY RADIATION

The nonresonant molecules and the nonresonant degrees of freedom (for the sake of argument, we shall refer hereafter only to molecules) do not interact directly with the radiation. Resonant molecules absorb photons of energy $\hbar\omega_l$ and are then deactivated, injecting this energy into the surrounding medium and heating it. We emphasize that the medium is heated only by deactivation acts that are localized in time and in space. Each deactivation of a resonant molecule is accompanied by a rise in the temperature of its ambient. The activated region (AR) so produced has a short lifetime, since the size of the AR is rapidly increased by heat conduction and the temperature in it is lowered. The local temperature $T(t,\mathbf{r})$ at an arbitrary point is therefore practically never much different from the average temperature $\overline{T}$. However, $T(t,\mathbf{r})$ can nevertheless exceed $\overline{T}$ substantially if deactivation took place recently near the point $\mathbf{r}$, i.e., if the point $\mathbf{r}$ is located in the AR.

Even though the total volume of all the AR at each instant of time is much smaller than the volume of the medium, the temperature excess in the AR can be large enough for chemical reactions with sufficiently high activation energy, as well as for all other processes whose rate increases rapidly with temperature, to proceed mainly in the AR.

EFFECT OF ACTIVATED REGIONS

Consider a medium consisting of passive molecule (marked p), resonant molecules that absorb the laser radiation (marked l), and reacting molecules that decay with increase in temperature (marked r). We denote their densities by

$$n_{p,l,r}=c_{p,l,r}n,$$

where $n=n_p+n_l+n_r$; c_p, c_l, and c_r are the corresponding dimensionless densities. The rate ν of decay of the reacting molecules depends on the temperature of the medium in accord with the Arrhenius law

$$\nu=K\exp[-E_a/T],$$

where E_a is the activation energy. In ordinary heating, not more than

$$w_T=vtnc_rK\exp[-E_a/T_m]$$

reacting molecules decay in a time t and in a volume v (T_m is the maximum temperature possible under the experimental conditions).

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When heated by radiation, a volume v absorbs $vtnc_lJ\sigma$ photons in a time t, where σ is the absorption cross section and J is the photon flux density (we assume that the radiation penetrates through the entire volume v and little of it is absorbed). Each absorbed photon produces after a certain time one AR. Let $T(t)$ be the temperature at the center of the AR and $N(t)$ the characteristic number of molecules in this region (see below). In each AR there are decayed

$$c_rK\int_0^{t_1} dtN(t)\exp\left[-\frac{E_a}{T(t)}\right] \tag{1}$$

reacting molecules. Here t_1 is the lifetime of the AR; we do not need an exact definition of t_1, since it will be found that all the quantities of interest to us are practically independent of t_1. Thus, heating by radiation produces the decay of only

$$w_l=vtnc_lc_rJ\sigma K\int_0^{t_1} dtN(t)\exp\left[-\frac{E_a}{T(t)}\right] \tag{2}$$

reacting molecules.

We calculate now the integral in (1) and (2). The quantities $T(t)$ and $N(t)$ are connected by the relation

$$\hbar\omega_l+CN(t)T_m=CN(t)T(t), \tag{3}$$

which expresses the energy conservation law. Here C is the characteristic dimensionless heat capacity per molecule (usually $C=5$ to 10 for liquids). Assuming that the spreading of the AR is due to thermal conductivity, we put

$$N(t)={}^4/_3\pi n(4\chi t)^{3/2}, \tag{4}$$

where χ is the thermal diffusivity coefficient.

We introduce the ratio $R=w_l/w_T$, which characterizes the relative role of the temperature microfluctuations. Using (3) and (4), we obtain

$$R=\frac{1}{6}\left(\frac{3}{4\pi}\right)^{2/3}\frac{c_lJ\sigma}{n^{2/3}\chi}\left(\frac{\hbar\omega_l}{CE_a}\right)^{5/3}\exp\left[\frac{E_a}{T_m}\right]S, \tag{5}$$

where

$$S=\int_{x_0}^{x_1}\frac{dx\,x^{2/3}e^{-x}}{(1-T_mx/E_a)^{5/3}},\quad x=\frac{CE_aN}{\hbar\omega_l+CT_mN}, \tag{6}$$

with $x+x_0$ when $N=N(t=0)$ and $x=x_1$ when $N=N(t=t_1)$. $N(0)$ should be taken to mean the minimum number of particles in the AR, starting with which, i.e., at $N\geqslant N(0)$, a macroscopic description of the AR is possible [see Eq. (4)].

In order of magnitude we have $N(0)\sim\sigma_t^{-1}n^{-2/3}$, where σ_t is the transport cross section. In rarefied gases this number can be very large, and in liquids and in other dense media $N(0)\sim1$. We shall consider below only dense media. Since the number $N(T_1)$ is very large, we have $x_1\approx E_a/T_m$. In all cases of real interest

$$E_a/T_m\gg1,\quad \hbar\omega_l/T_m\gg1. \tag{7}$$

The integrand in (6) is always nonsingular. By virtue of the second inequality in (7) we can assume the denominator of (6) to be equal to unity and replace x_1 by ∞. We confine ourselves first to the case of hard photons, when

$$CE_a/\hbar\omega_l\ll1. \tag{8}$$

Since $N(0)\sim1$, we have $x_0\ll1$ [see (7) and (8)]. Putting $x_0=0$, we find that the integral (6) is equal to $S=\Gamma(5/3)$, where Γ is the gamma function.

In the case of soft photons, when an inequality inverse to (8) holds, we have $x_0\gg1$. Hence

$$S={}^2/_3x_0^{2/3}e^{-x_0}. \tag{9}$$

We note that expression (5) is valid for R only if it turns out that $R\gg1$.

DISCUSSION

When a medium is heated by radiation, it is precisely the microfluctuations of the temperature which determine the rate of the chemical reaction if $R\gg1$. The quantity T_m in (5) has then the meaning of the material temperature averaged over the time and (or) space. Let us make some numerical estimates. Let the medium be water; it is then reasonable to assume that $T_m=100$ °C $=373$ K; the density $n=3.3\times10^{22}$ cm^{-3}, the thermal diffusivity $\chi=1.8\times10^{-3}$ cm^2 sec^{-1}, and the heat capacity $C=8.3$. Let $\hbar\omega_l=6\cdot10^4$ K ($\lambda=2\pi c/\omega_l\approx250$ nm), the absorption cross section $\sigma=10^{-19}$ cm^2, and the irradiance $I=\hbar\omega_lJ=3\cdot10^8$ W/cm^2. So large in irradiance is compatible with the low temperature $T_m=100$ °C because the laser pulse can have a short duration or, for example, because water is rapidly cooled by the walls of the capillary in which it is contained. UV radiation with $\lambda=250$ cm is well absorbed by the water itself, so that we can put $c_l=1$. The ratio R is then noticeably larger than unit when $E_a\geqslant10$ kcal/mol. We note that this estimate depends little on all parameters except T_m, since (5) contains a large exponential factor. The conditions considered correspond to the case of hard photons. When the energy $\hbar\omega_l$ is decreased we deal with soft photons. The energy E_a is then increased, since $S\ll1$ [see (9)], but this increase is negligible because the conditions (7) are satisfied.

The exponential Arrhenius factor in the AR will be noticeably larger than that for an average temperature T_m so long as the number N of particles in the AR is not too large, so that $NCT_m^2\lesssim\hbar\omega_lE_a$. It follows therefore that $N\approx10^3$ at $E_a=30$ kcal/mol. This number of particles corresponds to a size 2×10^{-7} cm and a time 10^{-11} sec. These quantities can be regarded as the characteristic size of the characteristic lifetime of the AR when the spreading of the AR is due to heat condition.$^{1)}$

The ratio R increases rapidly with increasing E_a. In other words, the action of the heating the medium by UV radiation is selective in the sense that the relative increase of the rate of the chemical reaction is stronger the higher its activation energy. (It is of interest to note that such a phenomenon was deduced theoretically in Refs. 3 and 4, but in a different physical situation, when reactions with participation of resonant molecules were stimulated.) Thus, by using UV to heat a dense medium, and experimenter can observe, for example, the onset of decay of even stable molecules that do not absorb the radiation, even though the average temperatures of the medium is not greatly raised.

We point out in conclusion that chemical reactions can be influenced by fluctuations not only when radiation is absorbed. Thus, for example, a nontrivial influence of thermodynamic fluctuations of the density on the kinetics of the approach to equilibrium was observed in Refs. 5 and 6.

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(1) Deactivation can lead in principle to an expanding shock wave. In this case the AR is a spherical shell with increased temperature and density against the background of the shock wave. The effect of the AR depends in this case strongly on the deactivation conditions.

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