

The existence of micrometeorite craters on meteoritic materials provides a means of studying properties of the dust component of the ancient solar system. On the basis of the work presented here, it appears that, although the flux may have been slightly higher in the past, the size distribution and physical properties of the interplanetary dust have not changed appreciably over most of the age of the solar system. Because it is generally believed that interplanetary grains are derived from comets, this implies a long-term stability to cometary phenomena in the inner solar system.

Note added in proof: From discussions with Noonan and Jeromé (18), we have learned that chondrule-like objects have recently been found in two other howardites: Bununu and Malvern.

D. E. BROWNLEE

Department of Astronomy, University of Washington, Seattle 98195

R. S. RAJAN

Department of Physics, University of California, Berkeley 94720

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Quantum Low-Temperature Limit of a Chemical Reaction Rate

Abstract. *The radiation-induced polymerization of formaldehyde has been studied in the solid state. The time of addition of one new link to a polymer chain increases exponentially in accordance with the Arrhenius law at 140 to 80 K, but approaches a constant value (approximately 10^{-2} second) at temperatures below 10 K. Thus, a low-temperature limit to a chemical reaction rate has been observed. It is interpreted as a quantum effect caused by tunneling from the zero vibration level of the initial state, and a semiquantitative theory is given. The phenomenon should be taken into account for understanding tunneling of electrons in biological systems when such tunneling is accompanied by conformational changes. It could also be significant in slow, exothermic chemical reactions at low and ultralow temperatures, which may have had a role in chemical and biological evolution (cold prehistory of life?).*

In a number of experiments (1) we have determined calorimetrically the time of growth of polymer chains for the radiation-induced solid state polymerization of formaldehyde at low temperatures (4 to 140 K). The polymerization at 77 to 140 K was induced by the bremsstrahlung of 5-Mev electrons from a linear accelerator; an adiabatic calorimeter with a relaxation time of 0.3 to 0.5 second was used. Below 77 K polymerization was induced by ^{60}Co gamma rays passing through a lead shield by means of a slit with a short opening time; the relaxation time of the diathermic calorimeter with Cu-Au-Fe thermocouples was 1 to 2 seconds.

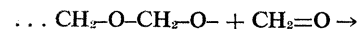
Judging from the large radiation yields of polymerization ($G = \sim 10^7$ molecules per 100 ev at 140 K, $\sim 10^5$ at 77 K, and $\sim 10^3$ at 4 K), the role of radiation seems to be restricted to the formation of primary active centers—that is, to starting the polymer chain (which is endothermic). Once the chain starts, the formation of each new link is an exothermic process which can proceed spontaneously, without the participation of radiation.

The results are represented in Fig. 1, where $\tau_0 = \tau/G$ is the average time of addition of one new link to a polymer chain (τ is the measured time of growth of a whole chain, and the radiation yield of chain initiation is taken as ~ 1 for all temperatures). When the temperature decreases from 140 to 80 K, the value of τ_0 increases in accordance with the Arrhenius law with an activation energy $E \approx 0.1$ ev. At lower temperatures, however, we observe a strong deviation from the Arrhenius law and τ_0 approaching a constant value of approximately 10^{-2} second. An Arrhenius-type extrapolation would give a τ_0 of about 10^{30} years for 10 K and about 10^{100} years for 4 K.

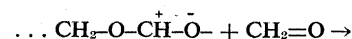
Thus, a low-temperature limit to a

chemical reaction rate has been observed for the radiation-induced polymerization of formaldehyde. Such a limit can only be of quantum origin, caused by tunneling from the zero vibrational level of the initial state. Also, such transitions are impossible for endothermic reactions.

Tunneling between two equal potential wells without a change of the system's energy has been treated for a Boltzmann continuous distribution and a quantum mechanical distribution (2). It was shown that for these simplified cases the reaction rate at low temperatures should reach some plateau value, determined by the parameters of the potential barrier (height, width, and shape) and by the tunneling mass. However, our present experimental case is more complicated because it involves transitions between two different wells, as illustrated in Fig. 2. Two effects must happen to establish a new link of the polymer chain: the molecule of formaldehyde must get closer, with the C-C distance changing from d_i to d_f ($d_i - d_f = \Delta d$), and the C=O bond must change from a double bond to a single bond. The growth of the polymer chain should involve either the transfer of an electron



or the transfer of a hydrogen atom



but in any case the transfer should be accompanied by (or should lead to) the approach of the formaldehyde molecule to the end group of the growing polymer. The tunneling of the whole formaldehyde molecule (mass M) is certainly much slower than electron tunneling, because of the large difference in their masses: $M/m \approx 5.5 \times 10^4$. It is not as easy to exclude

proton tunneling as a rate-determining step, because such tunneling for a distance d_0 can be as slow as a formaldehyde tunneling for a distance Δd much less than d_0 . However, we recently compared the polymerization rates for ordinary formaldehyde and deuterated formaldehyde at about 4 K and found no marked difference; therefore the tunneling of the entire formaldehyde molecule is the rate-determining step.

Let us treat the addition of the formaldehyde molecule to the growing polymer chain in terms of the quantum theory of relaxation processes developed in (3-5).

In the adiabatic approximation various states of formaldehyde molecules are represented by the potential curves shown in Fig. 2. Initially states b_1 and b_2 are occupied and potential well a is vacant. In the adiabatic approximation such a situation would correspond to a stationary state (neglecting the very low rate of radiative transition $b_1 \rightarrow a$). However, because of the existence in the Hamiltonian of the so-called nonadiabaticity operator—that is, of a higher term of the Born-Oppenheimer parameter $\mathcal{H} = (m/M)^{1/2}$ —there occurs relaxation of the system with transition of formaldehyde from the well b_1 to the deeper well a at a distance Δd (the elementary step of the polymer chain growth). The next formaldehyde molecule can then pass from b_2 to the empty well b_1 , with subsequent addition to the polymer chain ($b_1 \rightarrow a$), and so forth. The probability of a $b_1 \rightarrow a$ transition can be estimated [for example, see (3)] as

$$W_{ot} = \frac{2\pi}{\hbar} L_e^2 F_{v_i v_f} \rho_f \quad (1)$$

where $L_e = \int \Psi_i L \Psi_f d\tau_e$, Ψ_i and Ψ_f being the adiabatic electron wave functions of the initial and final states and L the operator of nonadiabaticity; $F_{v_i v_f}$ is the Franck-Condon factor

$$F_{v_i v_f} = \left| \int \varphi_{v_i}^{(i)}(q) \varphi_{v_f}^{(f)}(q) dq \right|^2$$

and $\rho_f \sim 1/\hbar\omega_f$ is the density of vibrational levels in the final state. From the properties of L it follows that $|L_e/\hbar\omega_e| \sim \mathcal{H}^3$ where ω_e is the characteristic frequency of electron transitions ($\omega_e/2\pi \sim 10^{15}$ sec $^{-1}$).

The Franck-Condon factor for $v_i = 0$ is expressed as (4)

$$F_{0, v_f} = \frac{1}{2^{v_f} v_f!} \exp\left(-\frac{2}{1+\beta^2} y_f^2\right) \times \frac{2\beta}{1+\beta^2} \left| \frac{1-\beta^2}{1+\beta^2} \right|^{v_f} H_{v_f}^2 \left(\frac{2^{1/2} y_f}{|1-\beta^2|^{1/2}} \right) \quad (2)$$

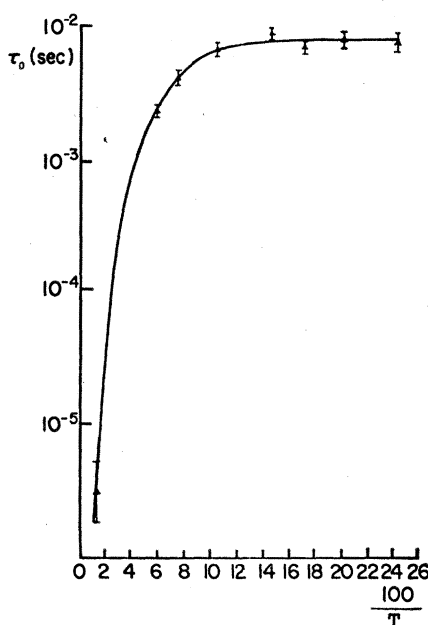
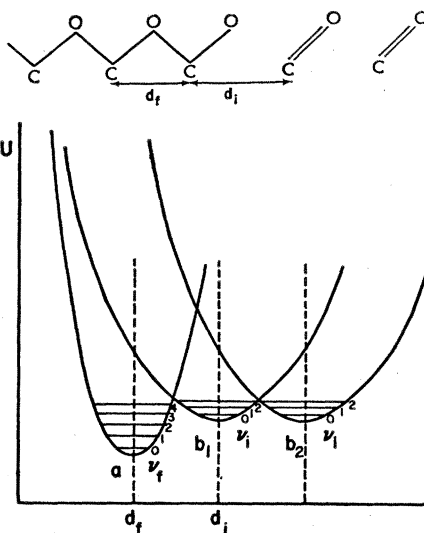


Fig. 1. The average time (τ_0) of addition of one new link to a polymer chain versus 100 over temperature (T).

where $\beta = (\omega_f/\omega_i)^{1/2}$, $Y_f = \Delta d(M\omega_f/2\hbar)^{1/2}$, and H_{v_f} is a Hermite polynomial.

The vibrational frequency of formaldehyde groups in a polymer chain can be estimated roughly as $\omega_f \approx 2\pi c \times 1000$ sec $^{-1}$, whereas $\omega_i \approx 2\pi c \times 100$ sec $^{-1}$ ($\omega_i < \omega_f$). Furthermore, $v_f \approx Q/\hbar\omega_f \approx 2$ to 3, where Q is the heat of polymerization, experimentally determined by us as approximately 0.37 eV. Taking from experiment (see Fig. 1) that $W_{ot} \sim 10^2$ sec $^{-1}$ —that is, that at $(2\pi/\hbar)L_e^2 \rho_f \approx 10^{11}$, $F_{03} \approx 10^{-9}$ —we find that for a given interval of ω_i , $y_f \approx 8$ to 9; that is, $\Delta d \approx 0.4$ to 0.5 Å. This value seems to be reasonable (we



were unable to find experimental data about the difference in C-C distances between formaldehyde and polyformaldehyde).

Either the growth of the polymer chain ($b_1 \rightarrow a$ transition) or the transport of monomer molecules to the cavities formed during the polymerization ($b_n \rightarrow b_{n-1}$ transitions) can determine the rate of low-temperature solid state polymerization. But both processes are of quantum origin, being caused by the tunneling of entire reacting formaldehyde molecules from zero vibrational levels. Thus, what is described here is the quantum limit of the rate of a chemical reaction in the full sense of these words, including changes of interatomic distances, chemical bonds, and valence angles—unlike the cases of low-temperature electron tunneling reported previously (6). The treatment given here can be extended to higher temperatures. In this case a Boltzmann distribution leads to the Arrhenius law (2).

The detailed study of the low-temperature limit of chemical reaction rates is of fundamental significance. It should be taken into account for understanding tunneling of electrons in biological processes, when such tunneling is accompanied by relaxation type conformational changes [for example, see (7)]. Furthermore, near absolute zero entropy factors play no role, and all equilibria are displaced to the exothermic side, even for the formation of highly ordered systems. Therefore it would be of interest to establish the role of slow chemical reactions at low and ultralow temperatures in chemical and biological evolution (cold prehistory of life?).

V. I. GOLDANSKII
M. D. FRANK-KAMENETSKII
I. M. BARKALOV

Institute of Chemical Physics, U.S.S.R.
Academy of Sciences, Vorob'yevskoye
Shausse, 2-B, Moscow, B-334

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