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Kinetics of azobenzene nitrene oxidation by molecular oxygen in glassy propylene carbonate

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The kinetics of azobenzene nitrene oxidation by molecular oxygen dissolved in a matrix was studied in glassy propylene carbonate. The reaction was carried out in excess oxygen within its concentration range 0.008 to 0.048 M. The oxidation kinetics, controlled by oxygen diffusion, is not described by the exponential function. A specific reaction rate decreases in the course of the process. The higher the oxygen concentration in the matrix, the sharper is the decrease in the reaction rate. It is shown that at all concentrations, the oxidation kinetics is described in the framework of the model of heterogeneous matrix with a characteristic size of heterogeneities of 1.5 nm and a dispersion of the activation energy of oxygen molecule jump of 4 kJ/mol. The reaction radius is about 0.5 nm. © *2011 American Institute of Physics*. [doi:10.1063/1.3671637]

I. INTRODUCTION

In organic low-molecular weight and polymeric glasses, the oxidation kinetics of free radicals $\dot{R} + O_2 \rightarrow R\dot{O}_2$ and nitrenes $R\ddot{N} + O_2 \rightarrow RN\ddot{O}_2$ is controlled by oxygen diffusion (see, e.g., Refs. 1–6). Oxygen concentration in a matrix is usually much higher than that of reactive particles. Despite the pseudo-first order of the reaction, its kinetics is commonly not described by an exponential function.[1–6] A specific reaction rate decreases during the process, often by several orders of magnitude. The reason of the reaction rate decrease is the glass heterogeneity. The rate of diffusion-controlled processes is the frequency of the encounters of reacting particles.[7] Its value depends on the translational mobility of oxygen near the immobile reagent. The mobility of gas molecules is sensitive to the local matrix density. Because of differences in the environment, the oxidation rate constant is different for different particles. In the beginning of the process the particles with higher rate constants react with oxygen, while the particles with lower rate constants oxidize later. As a result the kinetics is stretched over a broad time range. This kinetics may be described in terms of oxygen diffusion characteristics on a nanometer length scale which is the focus of attention of the present work.

In glasses, there are numerous cavities of the atomic length scale.[8,9] It is assumed that the small molecules, such as oxygen, diffuse due to the thermally activated jumps from one cavity to another.[8,10–12] Since this diffusion is decoupled from the cooperative rearrangement of the matrix, oxygen has a high translational mobility even at temperatures much below the glass transition temperature T_g. Because of the structural disorder of glass, the height of the activation barrier between the neighboring cavities fluctuates in space over a wide range.[13]

As shown recently, the heights of barriers between the neighboring cavities in glassy propylene carbonate (PC) are spatially correlated.[14] The correlation length ξ is estimated as 1.5 nm. The value of ξ exceeds the average distance between the neighboring matrix molecules by a factor of three. It follows that in the regions consisting of about 30 PC molecules, the jump rates of oxygen molecules vary moderately, whereas between the neighboring regions, these may differ by two orders of magnitude (the dispersion of barrier energy σ is 4 kJ/mol at an average barrier height of 45 kJ/mol). The value of ξ is actually the characteristic size of the structural heterogeneities of a glassy matrix. These heterogeneities are likely to be the density fluctuations, frozen at T_g from the liquid state.[15] The heterogeneities were found to differ in density by 0.8%.[16]

The process kinetics, controlled by oxygen diffusion, is highly sensitive to ξ and σ.[14] Therefore, it is a suitable tool for studying the glassy matrix heterogeneities on a nanometer length scale. The present work studies the kinetics of triplet azobenzene nitrene oxidation in glassy PC. We have also calculated the kinetics of this process in the heterogeneous matrix with ξ and σ taken from Ref. 14. The reaction radius ρ was used as a free parameter in oxidation kinetics simulation. Agreement between experimental and calculated kinetic curves at reasonable ρ confirms the heterogeneous structure of the glassy PC, described in Ref. 14.

II. EXPERIMENTAL

Propylene carbonate (>99%) was purchased from Fluka and used as received. The glass transition temperature of PC is 158 K based on differential scanning calorimetry at a 10 K/min heating rate after quenching from the liquid state.[17] *p*-Phenylazophenyl azide C_6H_5–N_2–C_6H_4–N_3 was synthesized in our laboratory.[5]

The samples were prepared from the azide solution in PC with a concentration of 10^{-3} M in quartz ampoules 3 mm in inner diameter and 20 cm in height. A solution was saturated with oxygen at room temperature. Specially designed ampoules were used to saturate the samples with gas.[18] A

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solution was poured into the flask welded to the ampoule and connected to a gas cylinder with compressed oxygen. Saturation pressure was varied from 0.25 to 1.5 MPa. The liquid in the flask was degassed and stirred under oxygen for 45 min. Then the oxygen-saturated solution was poured out into the ampoule, frozen, and the ampoule was detached from the gas cylinder. The height of the sample was about 6 cm. The samples were frozen in two steps. At first, the lower part of the ampoule, 4 cm in height, was immersed in liquid nitrogen. The upper liquid part of the sample served as a plug to prevent oxygen exchange between the lower part of the sample and the gas phase. The remaining part of the ampule was frozen 40 s later.

The oxygen-containing samples were used together with those saturated with an oxygen/nitrogen mixture with a total gas pressure of 1 MPa. The partial oxygen pressure was 0.25 MPa.

The oxygen and nitrogen solubility in PC at room temperature obeys Henry's law with constants equal to $(1.74 \pm 0.03) \times 10^{19}$ m^{-3} Pa^{-1} for oxygen[14] and to $(1.02 \pm 0.04) \times 10^{19}$ m^{-3} Pa^{-1} for nitrogen. The gas concentration in glass was calculated taking into account the thermal expansion of PC.[16] In all the cases, the concentration of oxygen exceeded that of azide by no less than an order of magnitude.

The rapidly cooling samples were annealed at 152 K ($T_g - 6$ K) for 28 h. Annealing leads to almost equilibrium glass state.[19] At temperatures below 152 K, the structure relaxation times in annealed samples are much longer than 10 h.[19] As a result, the structure of these glasses did not vary either when sample cooling to experimental temperature (from 123 to 142 K) or during experiment, lasting for no longer than 10 h. This was verified experimentally. It is established that preliminary annealing for 30 h at experimental temperature has no effect on the nitrene oxidation kinetics. Thus, the matrix structure remains the same at all experimental temperatures and it is close to the equilibrium PC structure at 152 K.

Azobenzene nitrene was produced at 77 K by photodecomposition ($\lambda = 365$ nm) of *p*-phenylazophenyl azide[20,21]

$$RN_3 \rightarrow R\ddot{N} + N_2.$$

We have made sure that no radicals were formed in pure PC, irradiated at this wavelength. A 1 kW high-pressure mercury arc lamp (DRSh-1000) was used for irradiation. The required mercury spectrum line was isolated using standard sets of colored glass filters immersed into a 10-cm water bath in order to filter the thermal radiation of the lamp. The irradiation time was 40 min which was sufficient to decompose no less than 80% of azide.

The X-band EPR spectrum of azobenzene nitrene was recorded as an asymmetric line 120 G wide in the field of about 6300 G. These spectra are typical of triplet nitrenes.[22–24] The line shape is due to the randomly oriented triplets, for which the external magnetic field is perpendicular to the R–N bond.[25] The nitrene concentration in the sample was measured from the amplitude of this spectrum line. The signal was measured only in the bottom part of the sample 1.5 cm high. The spectra, in the form of the first signal derivative, were recorded at 77 K using an EPR-3 "Sibir" spectrometer (USSR). The microwave field power and the modulation amplitude were chosen so that the signal distortion was negligibly small. The signal intensity was normalized to the signal intensity of the $CuCl_2 \times 2H_2O$ reference sample placed in the cavity. The nitrene oxidation was carried in temperature-stabilized nitrogen flow. The sample temperature was kept constant to within 0.2 K.

III. RESULTS AND DISCUSSION

A. Experimental data

In oxygen-free samples, nitrenes are stable up to 160 K. When oxygen concentration is ≥0.008 M, nitrene lifetime at 140 K does not exceed 30 min. We assume that below 160 K the decay of nitrenes is determined by their reaction with oxygen.

Figure 1 shows the kinetic curves of nitrene decay for various oxygen concentrations. One can see that the reaction kinetics is not described by the exponential function. As the oxygen concentration increases, the reaction kinetics becomes more extended (the difference between the kinetic curves and the straight line becomes greater). This is

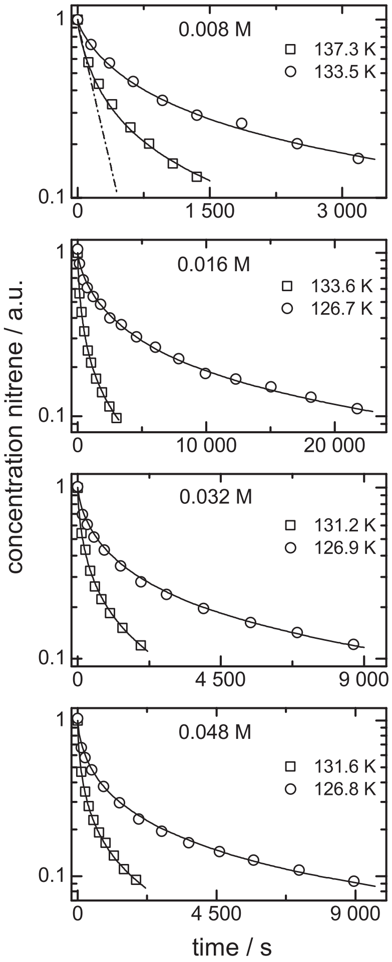

FIG. 1. The kinetics of nitrene oxidation by molecular oxygen in glassy PC matrix. Oxygen concentration and reaction temperature are shown. Solid lines are the best fits at $\xi = 1.5$ nm and $\sigma = 4$ kJ/mol, giving $\lambda = 0.52$ nm. Dash-dot line on the top panel is the kinetic curve calculated at $\sigma = 0$ and $P_0 = 0.5\ s^{-1}$.

typical of the diffusion-controlled reaction in the matrix with nanometer heterogeneities (see Ref. 14 and Sec. III B 1).

It is worth noting that in some quenched glasses, the oxidation rate of free radicals at low oxygen concentration ($<$0.01 M) increases with the addition of molecular nitrogen at a high concentration.[26–28] This effect is unobservable at high oxygen concentrations. The gas molecule energy in some cavities is believed to be substantially lower than that in other cavities. Oxygen molecules become embedded in these cavities and are not involved in radical oxidation. Nitrogen fills up the "deep" cavities increasing the number of mobile oxygen molecules. As a result, in the matrix with nitrogen, the rate of free radical oxidation is higher than that in the matrix without nitrogen. Nitrogen has no effect on the reaction rate at oxygen concentration, exceeding that of the deep cavities.

We studied the kinetics of nitrene oxidation for oxygen concentration 0.008 M in the matrix containing not only oxygen but also 0.014 M of nitrogen. In this case, there is no difference between these kinetic curves and those in the matrix containing only oxygen. Thus, in the glasses studied, the energy of gas molecules is actually the same in all the cavities.

B. The model of nitrene oxidation by mobile oxygen molecules in glassy PC

1. The factors determining radical oxidation kinetics controlled by oxygen diffusion in a heterogeneous matrix

In a heterogeneous matrix, the value of specific reaction rate depends on the location of radical. The reaction kinetics is characterized by radical distribution over specific rates (below the K-distribution). This distribution is very sensitive to reaction radius ρ, the heterogeneity length scale ξ, and the dispersion of barrier energy σ (the amplitude of heterogeneities).[14] To explain this sensitivity, we consider two cases: (i) ρ is much smaller, and (ii) ρ is much larger than ξ. In the first case, all the rates of oxygen molecule jumps about the reaction sphere of each radical are close to each other in value. Thus, the K-distribution reflects the distribution over the oxygen jump rates.[29] If $\rho > \xi$, the rates of the jumps over the reaction sphere surface are averaged and the K-distribution becomes narrower than that over the jump rates. Thus, the more the ρ/ξ ratio, the narrower is the K-distribution. At the same time, the wider the distribution over the jump rates, the wider is the K-distribution.

The oxidation kinetics at given ρ, ξ, and σ depends on oxygen concentration[14] because of the anomalous transport of gas molecules at short times (at small displacements of particles).[30,31] In the disordered matrix, the heights of the barriers between the neighboring cavities are different. Oxygen jumps mainly to a neighboring cavity separated by the lowest barrier. The real pathways of oxygen molecules at short times are the short sequences of the cavities separated by low barriers. The highest oxygen mobility is recorded within these sequences. A part of radicals is formed near such sequences. A radical is oxidized very rapidly when the neighboring sequences contain an oxygen molecule. A fraction of these radicals increases with oxygen concentration in the matrix. As a result, the higher the oxygen concentration in the matrix, the larger is the specific reaction rate at short times and the sharper is the decrease in this rate in the course of the process. At low oxygen concentration, the reaction proceeds mainly at times at which oxygen diffusion is Fickian.

2. Reaction radius

Under light, azide molecule decomposes into nitrene in the triplet state and a nitrogen molecule.[20,21] The reaction is irreversible. Nitrogen goes away into the bulk due to its high translational mobility at low temperature. After that, a cavity of several Angstrom in size remains, because the cooperative matrix restructuring, necessary for its destruction, is frozen. Therefore, the nitrene nitrogen atom is always adjacent to a cavity (below nitrene cavity) suitable for an oxygen molecule. The average distance between interstitial spaces in glassy PC is 0.5 nm. Thus, the distance between the nitrene cavity and the neighboring cavity that may contain oxygen molecule is equal, on the average, to 0.5 nm.

The oxygen jump in glassy matrices is a cooperative process. The cooperativity length scale is set by the size of the region with the spatially correlated elastic displacements of matrix molecules upon the formation of the channel between the cavities for oxygen diffusion. The jump probability is determined by the energy required to form the channel. The larger is the free volume in the region of the cooperative displacements of the matrix molecules, the lower is the value of this energy.

We assume that the probability of the jump of oxygen molecule into nitrene cavity is much higher than that of the jump into other cavities, because the nitrene cavity is best suited to an oxygen molecule due to the mechanism of nitrene formation. In this case, the oxygen molecule being in a neighboring cavity will most likely jump into nitrene cavity and nitrene will vanish. Thus, the reaction radius ρ is the distance between the nitrene cavity and the neighboring cavities. The nitrene oxidation rate is set by the frequency of oxygen entrance into these cavities. The value of ρ should be close to the average distance between the interstitial spaces in the matrix.

3. Computational procedures

A simple cubic lattice with the potential barriers of different height between the neighboring sites was used as a heterogeneous matrix model. The lattice sites are considered as the cavities for oxygen molecules. The barrier heights are spatially correlated. The energy barriers ε_{ij} between the sites i and j are random values taken from the distribution described by the Gaussian function

$$G(\varepsilon_{ij}) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\varepsilon_{ij}^2/2\sigma^2\right), \quad -\infty < \varepsilon_{ij} < \infty$$

with dispersion $\sigma = 4$ kJ/mol. A correlation function for ε_{ij} decays with increasing distance r between the barriers ε_{ij} and ε_{nm} as

$$C(r) = \frac{\langle \varepsilon_{ij}\varepsilon_{nm}\rangle}{\sigma^2} = \exp(-2r^2/\xi^2)$$

with correlation length $\xi = 1.5$ nm. Here, the brackets $\langle\cdots\rangle$ mean averaging over all the pairs of lattice barriers. The calculation procedure of the lattice with a spatial correlation of barrier heights is described in Ref. 14.

The Monte Carlo simulation of nitrene oxidation kinetics was performed using the lattice of $100 \times 100 \times 100$ sites with periodic boundary conditions. At the initial moment, 64 nitrenes were placed randomly in the lattice sites (cavities for gas molecules). The distance between nitrenes always is four times greater than the lattice constant. Oxygen molecules are distributed randomly over the remaining lattice sites. The number of the molecules corresponds to oxygen concentration in the glassy PC. Oxygen molecules diffuse due to thermally activated jumps into one of six nearest sites. The probability of encounters of oxygen molecules is low (a fraction of sites occupied by oxygen is below 0.004), therefore, we considered oxygen molecules to diffuse independently. The probability of a transition from site i to site j in a unit of time is defined by the equation

$$P_{ij} = P_0 \exp(-\varepsilon_{ij}/RT),$$

where the factor P_0 specifies the time scale for oxygen diffusion, R is the universal gas constant, and T is temperature. The calculation procedure for oxygen molecules walking in the lattice is described in Ref. 14. Nitrene was oxidized as soon as one of the oxygen molecules appeared in any of the six sites adjacent to this nitrene. In this case, the lattice constant λ is the reaction radius. The greater λ, the less correlated are the rates of the jumps of oxygen molecules into the reaction sphere of nitrene. As a result, the K-distribution becomes more narrow.

The lattice constant λ (the reaction radius) and factor P_0 are the free parameters; their values were chosen so that the simulated kinetic curve of nitrene oxidation could be most close to the experimental one. In the model, the mean height of the barriers $\langle\varepsilon_{ij}\rangle = 0$. The dependence of P_{ij} on the average energy of the real barriers is included in P_0. The oxidation curves presented are the averages over 2000 curves calculated for different lattices.

4. Nitrene oxidation kinetics

The dash-dot line in Fig. 1 represents the kinetic curve calculated in a homogeneous lattice ($\sigma = 0$, $\lambda = 0.52$ nm) at oxygen concentration of 0.008 M and $P_0 = 0.5$ s^{-1}. For this value of factor P_0, the decay time of 40% nitrenes (about 100 c) coincides with that of 40% nitrenes in PC matrix at 137.3 K. As one can see in Fig. 1, the kinetics of nitrene oxidation in homogeneous matrix is well described by the exponential function, which is the reason why the calculated and experimental kinetic curves dramatically diverge with increasing time.

Solid lines in Fig. 1 represent the result of the best fitting of all experimental data with the proposed model at $\lambda = 0.52$ nm. The standard error for λ is 0.02 nm. It is seen that the experimental data are well described by the model. The λ value is close to the average distance between the cavities in the matrix as it should be in our model of nitrene oxidation. The characteristics of heterogeneities ξ and σ are temperature independent, because the matrix structure remains the same at all experimental temperatures.

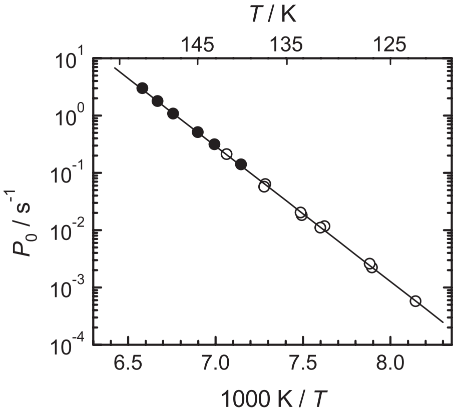

FIG. 2. Arrhenius plot of factor P_0 obtained from the kinetics of nitrene oxidation (open circles) and phenanthrene deactivation (solid circles, data from Ref. 16). The straight line denotes the linear fitting.

Figure 2 shows the fitted values of P_0, obtained from the description of the kinetics of both nitrene oxidation and phenanthrene deactivation by molecular oxygen.[14,16] The temperature dependence of P_0 was found to obey the Arrhenius equation $P_0(T) = A\exp(-E/RT)$ with $A = (1 \pm 0.2) \times 10^{16}$ s^{-1} and $E = (45.5 \pm 1)$ kJ/mol. The value of E corresponds to the average barrier height.

5. The effect of reaction radius on reaction kinetics: A test of the model

Figure 3 shows the kinetics of nitrene oxidation and phenanthrene deactivation by molecular oxygen in the glassy PC matrix. Oxygen concentration is the same in both cases. It is apparent that the K-distribution in the case of nitrene oxidation is much wider than that in the case of phenanthrene deactivation. The matter is that phenanthrene deactivation suggests no direct contact between phenanthrene and oxygen molecules. For this process, the Perrin radius is about

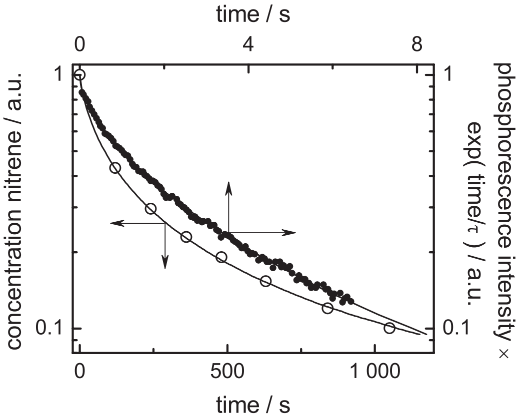

FIG. 3. The kinetics of nitrene oxidation at 137 K (open circles) and the kinetics of phenanthrene deactivation by molecular oxygen at 152 K (solid circles, data from Ref. 14) in glassy PC matrix. The oxygen concentration is 0.016 M and τ is the inherent lifetime of excited phenanthrene. The lines are the best fits at $\lambda = 0.52$ nm, $\xi = 1.5$ nm, and $\sigma = 4$ kJ/mol.

1.2 nm,[32,33] which is two times as large as the size of either phenanthrene or PC molecules. Therefore, oxygen can deactivate phenanthrene when being beyond its first coordination sphere. The radius of phenanthrene deactivation sphere is almost twice as large as that of nitrene oxidation. The rates of oxygen molecules jumps at opposite sides of the deactivation sphere correlate weaker than in the case of the oxidation sphere. As a result, the averaging of the jump rates over the deactivation sphere surface occurs and the *K*-distribution becomes narrow.

The lines in Fig. 3 represent the result of the best fitting of experimental data for both of the processes at $\lambda = 0.52$ nm, $\xi = 1.5$ nm, and $\sigma = 4$ kJ/mol. As follows from Fig. 2, at the same temperature, the value of P_0 factor is the same for both nitrene oxidation and phenanthrene deactivation. Thus, the kinetics of both processes is described in terms of the same characteristics of matrix heterogeneities.

C. On connection between structural and dynamical heterogeneities

The dynamics of molecules in deeply supercooled liquids and amorphous polymers in the rubbery state is spatially heterogeneous.[34–36] The term dynamical heterogeneity is used to refer to the presence of regions with different molecular mobility in a supercooled liquid.[37] 4D CP NMR experiments[38] show that the size ξ_{HD} of regions with molecular reorientation times longer than the average time falls in the range from 1 to 4 nm for various glass formers.[39,40] The regions of this size consist of several tens of molecules (or monomer units). With time, the region of high mobility can transform into the region of low mobility and vice versa. The lifetime of the regions is on the same time scale as cooperative reorientation of molecules[41–47] (but see Ref. 48–51). Thus, the same matrix cooperative rearrangement leads to both the reorientation of molecules in the region of volume $\sim \xi^3_{HD}$ and the change in reorientation time of these molecules. It is assumed then that the length scale of cooperativity is also the length scale ξ_{HD} of heterogeneity in molecular dynamics. The regions with different molecular mobility can be considered as the smallest regions that can be rearranged independently from their surrounding.

The regions with different molecular mobility can be considered as spatial fluctuations in the density or the configurational entropy.[40,52–55] In this case, the fluctuations at distance ξ_{HD} from each other are statistically independent and their amplitude in the volume ξ^3_{HD} is a characteristic of these heterogeneities. As the temperature decreases, the lifetimes of the fluctuations increase sharply (along with the times of α-relaxation). It is often assumed that below T_g the fluctuations manifest themselves as the static heterogeneities in density[56] or in elastic constants.[57,58] Most likely, the structural heterogeneities probed by oxygen diffusion in glassy PC are due to fluctuations in structure, frozen at T_g from the liquid state.[15]

IV. CONCLUSIONS

We have studied the kinetics of triplet azobenzene nitrene oxidation in glassy PC with oxygen concentration in a matrix varying from 0.008 to 0.048 M. It is shown that at all oxygen concentrations, the oxidation kinetics is described in the framework of the model of the heterogeneous matrix with a characteristic size of heterogeneities of 1.5 nm and a dispersion of the activation energies of oxygen molecules jump of 4 kJ/mol. The reaction radius is determined by the distance between the interstitial spaces and amounts to about 0.5 nm.

The structural heterogeneities are likely to be either the density or the configurational entropy fluctuations frozen at T_g from the liquid state. These heterogeneities are the characteristic feature of the glassy state and determine, together with the reaction radius, the processes kinetics controlled by oxygen diffusion.

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