Electronic Supplementary Information

Spin Statistical Factor

in Electron Transfer to Oxygen Molecules

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Section S1. **Experimental and Methodological details**

Fluorescence decays from the studied solutions were detected using a nanosecond X-ray fluorimeter[1] (references are given below in this Section) operating in the single photon counting mode. The light was collected using optical bandpass filters to isolate the fluorescence of a fluorophore. The duration of the ionizing X-ray pulse with a quantum energy of ~20 keV was *ca.* 1 ns.

The low-viscosity alkanes used [*n*-hexane (99.8%), *n*-octane (99%), isooctane (99.5%), *n*-nonane (99%), *n*-decane (99%), and dodecane (99%)] were additionally purified by stirring with concentrated sulfuric acid, washing with water, drying, and passing through a 0.3–0.5 m column of activated alumina. Viscous alkanes, 2,2,4,4,6,8,8-heptamethyl nonane, and squalane were used as received from AcrosOrganics. *N,N,N',N'*-tetramethyl-*para*-phenylenediamine (TMPD, 99%, Aldrich) was sublimed in vacuum three times before use, and *para*-terphenyl (99%, Aldrich), diphenylacetylene (99%, Aldrich), carbon tetrachloride (99%), and *N,N*-dimethyl-4-(phenylethynyl)aniline (98%) were used as received. The solutions were initially degassed using repeated freeze–pump–thaw cycles. In the experiment with oxygen, the oxygen pressure over the solution was controlled with an error of ~5%. The temperature of the solutions was stabilized with an accuracy of about ±1 K.

S1.1 General approach

The approach used herein to measure the rates of oxygen-related processes, electron transfer reactions, and spin decoherence in RIPs was based on the analysis of relative changes in the radiation-induced fluorescence kinetics caused by external factors, such as magnetic or electric fields and additional charge acceptors, which quench the fluorescence due to the scavenging of geminate ions. Such relative changes were calculated as the ratios between fluorescence kinetics $I_{B,E,Q}(t)$ recorded in the presence of an external magnetic (B) or electric (E) field, an additional acceptor (Q), and the unaffected fluorescence kinetics $I_0(t)$.

The kinetics of recombination fluorescence excited with rapid formation of the geminate RIPs involving a fluorophore can be represented as follows:[2]

$$I_{B,E,Q}(t) = \frac{1}{\tau_{fl}} \cdot \int_{-\infty}^{t} dt' \cdot exp\left(-\frac{t-t'}{\tau_{fl}}\right) \cdot F(E,t')\rho_{SS}^{B}(Q,t') \cdot \varphi(Q,t')$$

(S1)

The indices indicate the possible presence of the factor being investigated. Here, $F(E,t)$ is the recombination rate of geminate ions, which is believed to be independent of the spin state of the RIPs in alkanes; $\rho_{SS}^{B}(Q,t)$ is the probability of finding a geminate RIP in the singlet spin state; $\varphi(Q,t)$ is the probability of formation of an electronically excited state upon recombination charge carriers, which can depend on time if charge acceptor Q is added; and τ_{fl} is the fluorescence lifetime of the fluorophore.

$F(E,t)$ is a function to approximate the recombination rate of the ion pair, which was assumed to be the same for spin-correlated and non-correlated RIPs. It was assumed that the recombination rate obeys[3,4]

$$F(E,t) \propto \frac{1}{(t_0+t)^{3/2}} \cdot exp\left(-\frac{eE^2\mu_{\Sigma} \cdot t}{1.1 \cdot 4k_BT}\right)$$

(S2)

where μ_{Σ} is the sum of the mobilities of the charge carriers composing the RIPs, k_BT is the Boltzmann energy, e is the electron charge, and the multiplier 1.1 in the denominator is a correction factor as determined by computer simulation.[4] The parameter $t_0 \sim 1$ ns was selected to achieve a visual similarity between the experimental $I(t)$ curves and those obtained with Eq. (S1). Changing this parameter by a factor of two did not noticeably affect the calculated curves of fluorescence decay kinetics.

S1.2 Reaction rate measurement

For spin-independent reactions, if $\varphi(0,t) = \varphi_0$, and no electronically excited states can be formed after the reaction with a quencher, then the quantum yield obeys[5]

$$\varphi(Q,t) = \varphi_0 \cdot \exp\left(-4\pi R_{eff}D \cdot (t + \frac{2R_{eff}\sqrt{t}}{\sqrt{\pi D}}) \cdot [Q]\right) \approx \varphi_0 \cdot \exp\left(-4\pi R_{eff}D \cdot [Q] \cdot t\right)$$

(S3)

Here, [Q] is the concentration of an added quencher, which should be lower than the fluorophore concentration for a more accurate measurement.

At a short fluorescence lifetime, the reaction kinetics can be determined using the ratio of the recombination fluorescence decays recorded after and before quencher addition:

$$\frac{I_Q(t)}{I_0(t)} \approx \exp\left(- 4\pi R_{eff} D \cdot [Q] \cdot t\right) = \exp\left(-\frac{t}{\tau_Q}\right) \tag{S4}$$

If the quenching reaction is spin-dependent, then $\varphi(Q,t)$ is of a more complicated form that also depends on the external magnetic field.[6]

However, if the kinetics of the quenching reaction is determined in zero magnetic field for typical aromatic radical ions, then a deviation from Eq. (S4) does not exceed 20% within the initial time range of about 10–15 ns. A barely visible manifestation of such deviations can be found in Figure S1(b) for diphenylacetylene solutions. In the case of TMPD, with a comparatively long fluorescence lifetime, such deviations are completely masked due to the convolution with the fluorescence decay function, as described by Eq. (S1). As a result, the characteristic quenching reaction time τ_Q can be estimated using Eq.(S4).

S1.3 Time-resolved magnetic field effect

In this study, spin coherence in geminate RIPs was monitored using the method of time-resolved magnetic field effect (TR MFE),[7-9] which is determined using the ratio $I_B(t)/I_0(t)$.

In the calculations of the TR MFE curves, the evolution of the population of the singlet state in high $\rho_{ss}^B(t)$ and zero $\rho_{ss}^0(t)$ magnetic fields for singlet-born RIPs can be described by the following equations:[8,9]

$$\rho_{ss}^B(t) = \frac{1}{4} + \frac{1}{4}e^{-\frac{t}{T_1}} + \frac{1}{2}e^{-\frac{t}{T_2}}G_c^B(t)G_a^B(t) \tag{S5}$$

$$\rho_{ss}^0(t) = \frac{1}{4} + \frac{3}{4}e^{-\frac{t}{T_0}}G_c^0(t)G_a^0(t) \tag{S6}$$

where the indices *a* and *c* refer to the radical anion and radical cation, respectively; $1/T_1 = 1/T_{1c} + 1/T_{1a}$ and $1/T_2 = 1/T_{2c} + 1/T_{2a}$ are the sums of the rates of spin–lattice and phase relaxation for radical cations and radical anions in a high field, respectively; $1/T_0 = 1/T_{0c} + 1/T_{0a}$ is the parameter to describe phase relaxation in zero field. The relaxation rates include, in particular, the contribution originated from spin-selective reactions and/or spin exchange with paramagnetic particles.

The functions $G(t)$ is determined using semiclassical approximation, as follows:[10]

$$G^0(t) = \frac{1}{3} \cdot [1 + 2 \cdot (1 - (\gamma \sigma t)^2) \cdot \exp[-(\gamma \sigma t)^2 / 2]] \tag{S7}$$

$$G^B(t) = \exp[-(\gamma \sigma t)^2 / 2]] \tag{S8}$$

where σ^2 is the second moment of the radical ion spectrum of Electron Paramagnetic Resonance (EPR) in the field units ($\sigma = \Delta H_{PP}/2$ for a Gaussian-shaped spectrum), and $\gamma = g\beta/\hbar$ is the electron gyromagnetic ratio. The form of these functions suggests that these become nearly time-independent after $t \sim 2/(\gamma\sigma)$.

In the multiparticle radiation spur, some radical ions recombine with ions originating from different primary ionization events. In this case, the functions $\rho_{SS}^{B,0}(Q,t)$ calculated using Eqs. (S5–S8) to be submitted to Eq. (S1) should be replaced by the following expression:[8,9]

$$\rho_{SS}^{0,B}(t) \Rightarrow \theta \cdot \rho_{SS}^{0,B}(t) + (1-\theta)/4 \tag{S9}$$

Here, θ is a semiempirical parameter to take into account the contribution of those RIPs that are not spin-correlated. Typically, in liquid alkanes, $\theta \sim 0.2$.

At a longer time, the time-resolved magnetic field effect can be represented as:

$$\frac{I_B(t)}{I_0(t)} \approx \frac{\theta \cdot \rho_{SS}^B(t) + (1-\theta)/4}{\theta \cdot \rho_{SS}^0(t) + (1-\theta)/4} \xrightarrow{t \to \infty} 1 + \theta \cdot \exp\left(-\frac{t}{T_1}\right) \tag{S10}$$

Thus, the ratio decays exponentially with the characteristic time of decay of spin coherence in the recombining spin-correlated RIPs. The spin-selective reaction of one of the partners of geminate RIPs results in the acceleration of both phase and spin–lattice paramagnetic relaxation of the geminate RIPs.[6]

The values of σ for the utilized radical ions are known from literature. These are 1.43 mT for the radical cations of TMPD;[11] 0.36 and 0.33 mT for the radical cations[12] and anions[13] of *para*-terphenyl, respectively; 1.2 and 0.37 mT for the radical cations and anions of *N,N*-dimethyl-4-(phenylethynyl)-aniline;[14] and 0.32 and 0.44 mT for the radical cations and anions of diphenylacetylene,[15] respectively. However, the TR MFE curves were in some cases modeled neglecting a contribution from radical cations of polyphenyl compounds. This is becasue at early times $t < 2/(\gamma\sigma)$, the TR MFE is determined by spin evolution in RIPs "radical anion/solvent hole". In the most of liquid alkanes, the solvent holes exhibit a narrow EPR spectrum due to a rapid degenerate electron exchange.[16]

S1.4 Diffusion coefficients of ions and solvated electrons

Diffusion coefficients of the radical ions and solvated electrons were calculated with the Nernst–Einstein relation $D_{ion} = \mu k_B T/e$ using their mobilities μ determined by the time-resolved electric field effect method.[3,4] For a fluorophore with a short fluorescence lifetime, the ratio between the fluorescence decays under nonzero $I_E(t)$ and zero $I_0(t)$ electric field obeys

$$\frac{I_E(t)}{I_0(t)} \approx \frac{F(E,t)}{F(0,t)} \approx exp\left(-\frac{eE^2(\mu_- + \mu_+)\cdot t}{1.1\cdot 4k_B T}\right)$$

(S11)

For polyphenyl aromatic radical ions, it was assumed that the radical anion mobility μ_- exceeded the radical cation mobility μ_+ by 10%.[17] The mobility of TMPD radical cations in alkanes was estimated using the semiempirical relation suggested in ref 18.

The typical error of mobility measurements was estimated to be about 10-15%. This error was significant only in the case of reaction of electron scavenging since the relative diffusion in reaction between molecular radical anions and oxygen molecules was dominated by oxygen diffusion determined independently. No dependence of charge carrier mobility on the presence of oxygen in solution was found (Figure S3).

S1.5 Oxygen solubility and diffusion coefficients

The oxygen concentration in alkanes was determined using literature data.[19] In several cases, linear extrapolation of the values of the Ostwald coefficient to the regions of low or high temperatures was used. The diffusion coefficient of oxygen in alkanes was calculated as

$$D_{O2}(T, \eta) = A \cdot T / \eta^{p} \tag{S12}$$

at $\log(A) = -7.878$ and $p = 0.553$ for n-alkanes[20] and $\log(A) = -7.844$ and $p = 0.537$ for squalane.[21] For CCl_4 in alkanes, $\log(A) = -8.798$ and $p = 0.755$.[22] Alkane viscosity for a particular temperature was determined using literature data.[23-25]

Possible systematic errors related to the fact that the values of diffusion coefficients or oxygen solubility in many cases had to be extrapolated beyond the range of direct measurements were not evaluated herein.

References to Section S1

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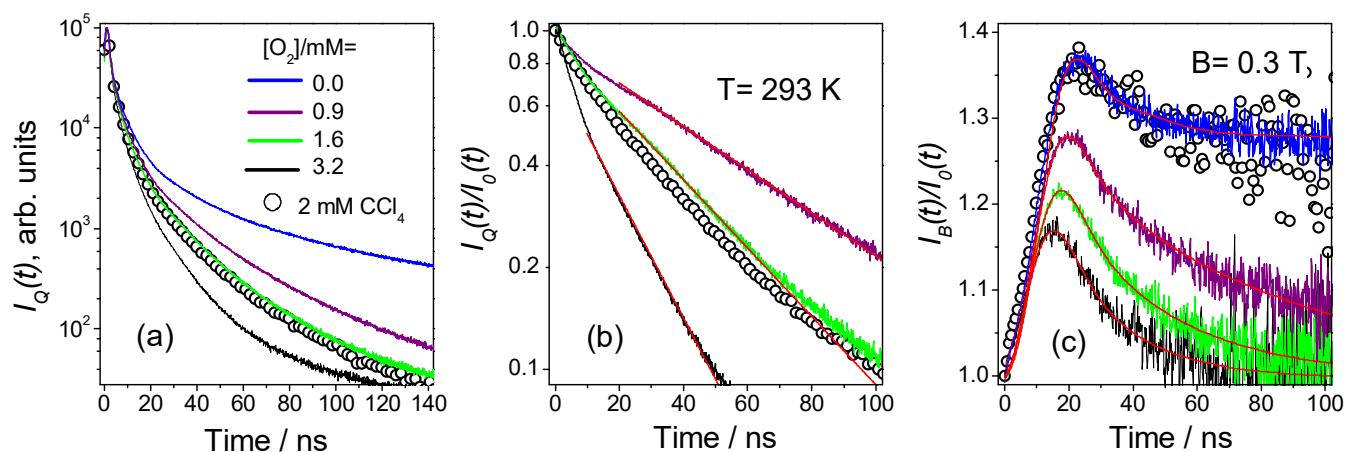
Figure S1. (a) Decays of the delayed fluorescence intensity $I_Q(t)$ for dodecane solutions of 20 mM diphenylacetylene at different concentrations of oxygen (lines) or CCl_4 (circles), T=293 K. Electron acceptors concentrations are indicated in the plot.

(b) Ratios $I_Q(t)/I_0(t)$ of the fluorescence decay kinetics measured after and before the addition of the quencher to the solution, respectively, for the same O_2 or CCl_4 nonzero concentrations as in (a). For $I_0(t)$, the upper curve in (a) is used. Solid red lines show exponential dependencies with characteristic times (top to bottom 67 ns, 42 ns, 22 ns).

(c) Ratios $I_B(t)/I_0(t)$ of the fluorescence decay kinetics measured, respectively, in strong (B = 0.3 T) and nearly zero magnetic fields for the same O_2 or CCl_4 concentrations as in (a). Solid lines show the calculated ratios obtained at T_1 values as indicated in the plot (top to bottom: 1000 ns, 68 ns, 41 ns, 22 ns).
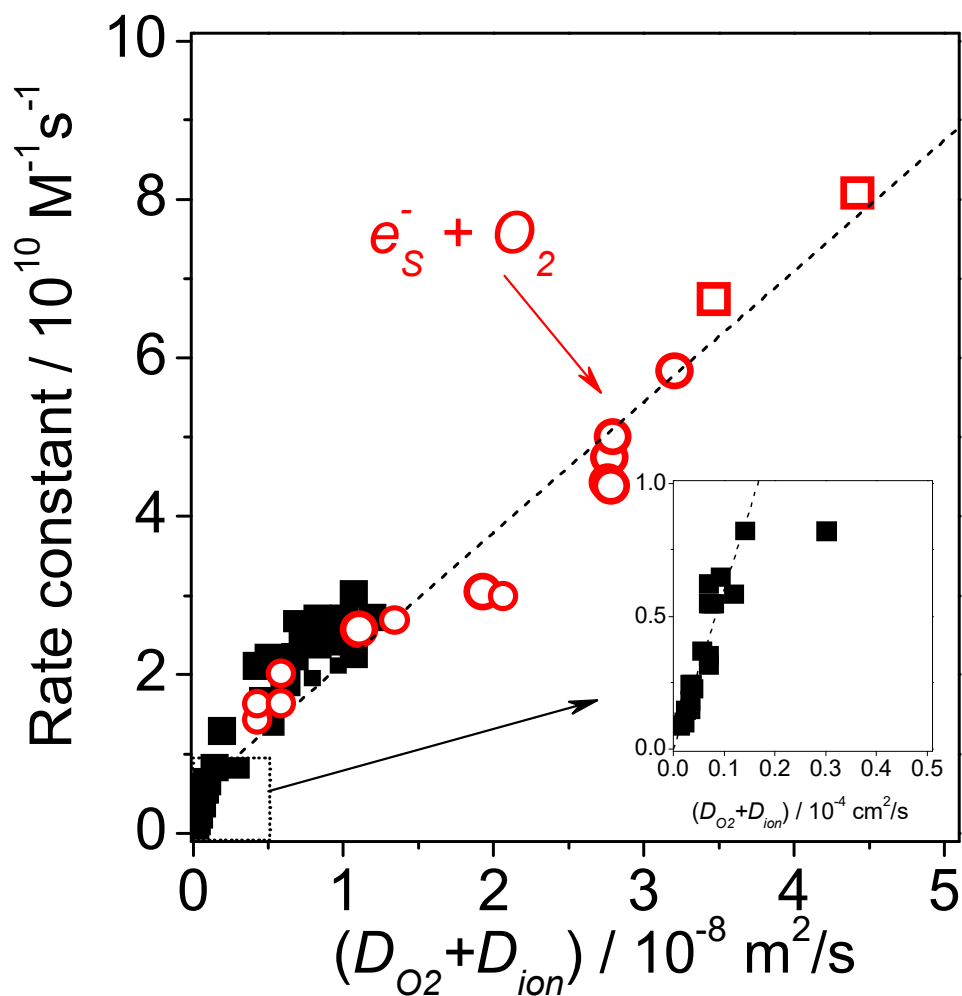
Figure S2. Rate constants for electron scavenging by oxygen in *n*-hexane (open squares), *n*-decane (circles), and for electron transfer from radical anions to oxygen in various alkanes (solid squares) vs. relative diffusion coefficient of the reactants within the temperature range 245-333 K. Slopes of the dashed lines in the main plot and in the insert differs approximately by 4 times.
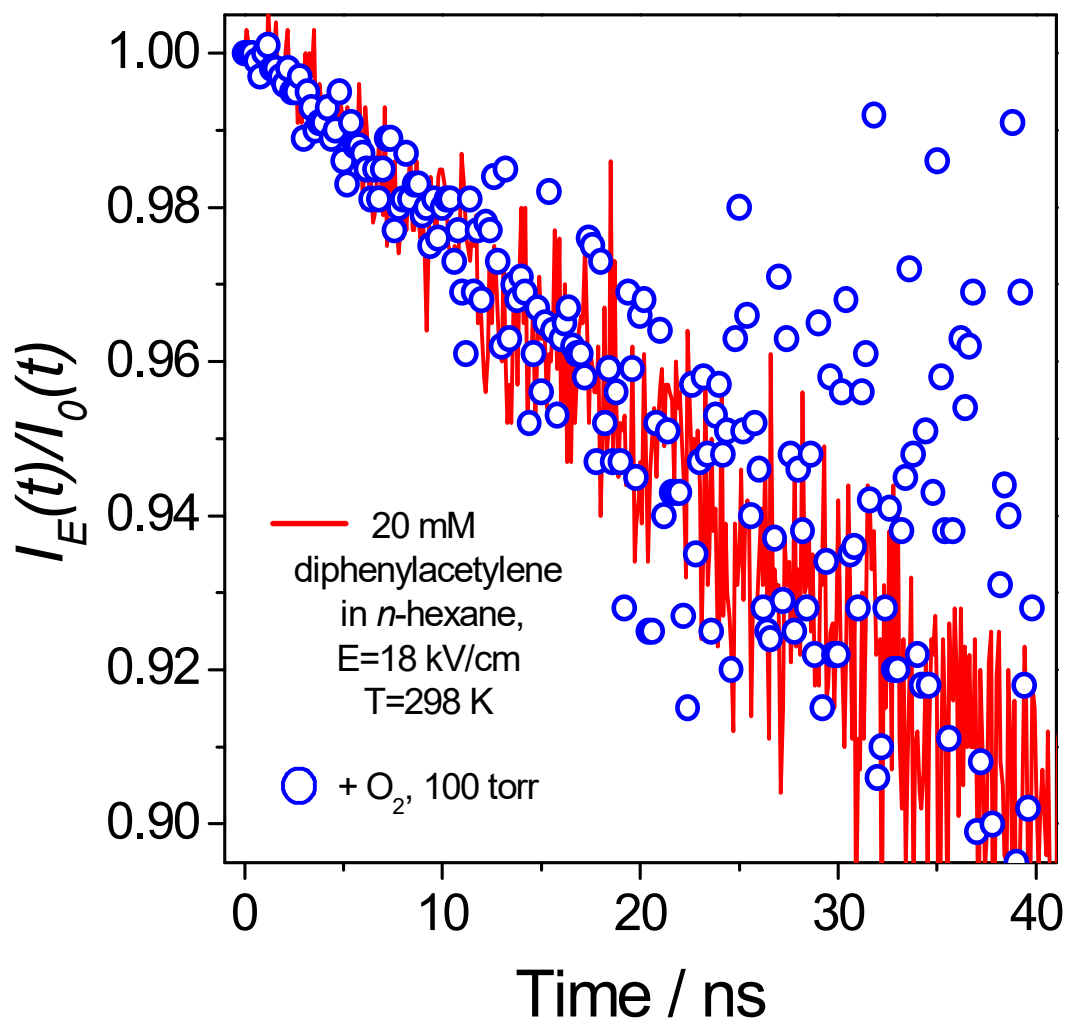
Figure S3. Ratios $I_E(t)/I_0(t)$ of the fluorescence decay kinetics measured, respectively, in external electric field E=18 kV/cm and nearly zero electric field, in the absence of oxygen (red line) and at O_2 pressure over the solution of 100 torr (circles). The slope of the curves of time-resolved electric field effect is nearly proportional to the relative mobility of recombining charge carriers.

Section S2

The rate of quartet-doublet transitions in encounter complex of two particles with spins $S_1=1/2$ and $S_2=1$

This section reproduces some important points of the solution of the problem as reported previously by Bagryansky et al. in J. Chem. Phys. 157, 064306 (2022); https://doi.org/10.1063/5.0101173

Consider a system consisting of two particles with spins $S_1=1/2$ and $S_2=1$ that can recombine from a doublet total spin state with a reaction rate constant k. In such a system we take into account isotropic exchange interaction with the exchange coupling J between the particles and dipole-dipole interaction in S_2. Then the equation describing the evolution of the density matrix of the system $\rho(t)$ is the following:

$$\dot{\rho} = -i[H, \rho] - \frac{k}{2}(P_d\rho + \rho P_d), \tag{S12}$$

where H is the Hamiltonian of the system, P_d is the projection operator on the doublet states $|d_{\pm 1/2}\rangle$ given in Eq. (S13):

$$P_d = |d_{1/2}\rangle\langle d_{1/2}| + |d_{-1/2}\rangle\langle d_{-1/2}| \tag{S13}$$

Denoting spin projection operators as S_{1x}, S_{1y}, S_{1z} and S_{2x}, S_{2y}, S_{2z}, the Hamiltonian of the system can be defined as the following:

$$H = J\left(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z}\right) + \tfrac{1}{3}D\left(2S_{2z}^2 - S_{2x}^2 - S_{2y}^2\right) \tag{S14}$$

In Eq. (S14), the Z-axis coincides with the principal axis of the zero field splitting tensor, and D denotes here the zero field splitting parameter.

As an initial state, here we consider the case of equal population of all spin states; therefore $\rho(0)$ is defined by Eq. (S15).

$$\rho(0) = \frac{1}{6}\hat{1}, \tag{S15}$$

where $\hat{1}$ is the identity operator.

The solution of Eq. (S12) with initial conditions Eq. (S15) can be obtained using the formalism of gyroscopic model [Merzbacher, E. *Quantum Mechanics.*

Wiley, New York, 1961]. The trace of obtained $\rho(t)$, which determines the fraction of pairs that have avoided the reaction by the time t, is the following:

$$Tr(\rho(t)) = \frac{1}{3} + \frac{1}{3[(\varepsilon_2-\varepsilon_1)^2+(\Gamma_2-\Gamma_1)^2]}\left\{e^{-2\Gamma_1 t}\left[\left(\varepsilon_2+\frac{D}{3}-\frac{J}{2}\right)^2 + \Gamma_2{}^2 + (\varepsilon_2+J)^2 +\right.\right.$$

$$\left.\left(\Gamma_2-\frac{k}{2}\right)^2 + \frac{4}{9}D^2\right] + e^{-2\Gamma_2 t}\left[\left(\varepsilon_1+\frac{D}{3}-\frac{J}{2}\right)^2 + \Gamma_1{}^2 + (\varepsilon_1+J)^2 + \left(\Gamma_1-\frac{k}{2}\right)^2 +$$

$$\frac{4}{9}D^2\right] - 2e^{-(\Gamma_1+\Gamma_2)t}\left[\left(\left(\varepsilon_1+\frac{D}{3}-\frac{J}{2}\right)\left(\varepsilon_2+\frac{D}{3}-\frac{J}{2}\right) + \Gamma_1\Gamma_2 + (\varepsilon_1+J)(\varepsilon_2+J) +\right.\right.$$

$$\left.\left.\left(\Gamma_1-\frac{k}{2}\right)\left(\Gamma_2-\frac{k}{2}\right) + \frac{4}{9}D^2\right)\cos(\varepsilon_1-\varepsilon_2)t\right]\right\} \tag{S16}$$

Where the parameters $\varepsilon_{1,2}$ and $\Gamma_{1,2}$ can be calculated as follows:

$$\varepsilon_{1,2} = \frac{1}{4}\left(-\frac{2}{3}D - J \pm \sqrt{\frac{\sqrt{x^2+y^2}+x}{2}}\right) \tag{S17}$$

$$\Gamma_{1,2} = \frac{1}{4}\left(k \mp \sqrt{\frac{\sqrt{x^2+y^2}-x}{2}}\right), \tag{S18}$$

at

$$x = 4D^2 + 9J^2 - 4DJ - k^2 \tag{S19}$$

$$y = 2k\left(\frac{2}{3}D - 3J\right) \tag{S20}$$

To analyze the case of relatively small values of the zero field splitting parameter D, the function, defined by Eq. (S16), should be expanded in terms of the small parameter $\frac{D}{|3J-ik|}$. Considering only the term with the small parameter at the minimal power, one can obtain that for $kt \gg 1$ population (S16) can be estimated as follows:

$$Tr(\rho(t)) \simeq \frac{1}{3} + \frac{1}{3}e^{-\frac{8D^2}{9(9J^2+k^2)}kt}\left(1 + \frac{16D^2}{9(9J^2+k^2)}\right) \tag{S21}$$

Eq. (S21) shows that for negligibly small values of $|D|$ with respect to $|J|$ and/or k, the quartet-doublet transitions are suppressed, and the population of the quartet state remains constant.

Section S3. Spin decoherence in a spin triad A-B-C due to spin-selective reaction in the pair B-C

Consider spin triad *A-B-C*, composed of spin ½ particles *A* and *B* and spin 1 particle *C* (triplet oxygen molecule). Let the initial state of pairs *A-B* correspond to the fraction of $0<\theta\leq1$ of the pairs in the singlet spin state, while the remaining pairs of fractions, $(1-\theta)$, as well as all radicals *C* are equally distributed over all possible spin states. In addition, particle *C* exhibits the paramagnetic relaxation caused by modulation by rotation of the DDI in the triplet particle.

Suppose that upon contact of particles *B* and *C* a spin-selective reaction between them occurs only from the doublet state of their total electron spin, and that this reaction is so fast that paramagnetic relaxation does not affect the reaction probability. Suppose also that the energy level splitting of doublet and quartet states, which are eigenstates for the Hamiltonian of exchange interaction in the pair *B-C* (see Eq. S3), is enough to consider the time-fluctuating DDI as a small perturbation. Also assume that the fluctuations are fast enough to satisfy the applicability of the Bloch-Wangsness-Redfield theory [Slichter, C. P. *Principles of Magnetic Resonance*. Berlin Heidelberg, Springer-Verlag 1990].

The density matrix of the initial state of the triad is equal to the product of the projection operator by the partially singlet state of the pair *A-B* by 1/3 of the unit operator $\hat{1}$ in the space of variables for *C*

$$\rho = \left(\frac{1}{4} - \theta\vec{a}\cdot\vec{b}\right)\frac{\hat{1}}{3}, \tag{S22}$$

where $\vec{a}$ and $\vec{b}$ are vectors composed of projection operators of spins *A* and *B* on the X, Y, Z axis. The density matrix describing the triad after reaction, is given by

$$\rho' = P_q\rho P_q = \frac{1}{12}P_q - \frac{\theta}{3}P_q\vec{a}\cdot\vec{b}P_q \tag{S23}$$

where P_q is the projection operator on the quartet states of the *B-C* pair which can be written using operators of projections of spins *B* and *C* as the following:

$$P_q = \frac{2}{3}\left(1 + \vec{b}\cdot\vec{c}\right) \tag{S24}$$

Eq. (S23) uses the projection operator property $P_q{}^2 = P_q$. As a basis, we choose the state vectors $|m, I, M\rangle$, where $m = \pm 1/2$ is the eigenvalue of the operator a_z, $I = (3/2, 1/2)$ is the value of the total spin of the pair B-C, and M is the value of its projection on the Z axis. The matrix elements of ρ' in this basis are equal to

$$\langle m, I, M | \rho' | m', I', M' \rangle =$$

$$\frac{1}{12} \delta_{mm'} \delta_{I3/2} \delta_{I'3/2} \delta_{MM'} -$$

$$\frac{\theta}{3} \delta_{I3/2} \delta_{I'3/2} \sum_{i=x,y,z} \langle m | a_i | m' \rangle \left\langle I = \frac{3}{2}, M \middle| b_i \middle| I' = \frac{3}{2}, M' \right\rangle \qquad (S25)$$

where δ_{ij} is the Kronecker symbol.

Suppose that during the reaction encounter of a B-C pair, probability of quartet-doublet transitions in this pair can be neglected (see Section S2). Oppositely, the spin mixing between quartet sublevels will be completed during the encounter due to stochastic DDI modulation. This means that in the density matrix (S25), the non-diagonal elements at indices M and M' will become equal to zero, and the diagonal elements (populations) will align with each other.

This will lead to the replacement in Eq. (S25) of the term $\left\langle I = \frac{3}{2}, M \middle| b_i \middle| I' = \frac{3}{2}, M' \right\rangle$ with an expression proportional to the state average with different value M of the value of the operator b_i of the spin projection B. Namely, with the expression $\delta_{MM'} \frac{1}{4} \sum_{M=-\frac{3}{2}}^{\frac{3}{2}} \left\langle I = \frac{3}{2}, M \middle| b_i \middle| I' = \frac{3}{2}, M \right\rangle$.

But these averages are equal to zero. This means that the matrix elements of the density matrix ρ'' transformed due to relaxation will be equal to

$$\langle m, I, M | \rho'' | m', I', M' \rangle = \frac{1}{12} \delta_{mm'} \delta_{I3/2} \delta_{I'3/2} \delta_{MM'} \qquad (S26)$$

A straightforward calculation verifies that the matrix elements (S26) correspond to the operator

$$\rho'' = \frac{1}{12} P_q = \frac{1}{18} \left(1 + \vec{c} \cdot \vec{b} \right) \qquad (S27)$$

where $\vec{c}$ is a vector composed of spin C projection operators. The state of pairs A-B is described by the density matrix

$$\rho_{AB}'' = Tr_c\rho'' = \frac{1}{6} \tag{S28}$$

corresponding to a complete decoherence of A-B pairs.

Section S4. Comparison between the rates of the reaction of pairs B-C and the spin decoherence in pairs A-B

Consider again a spin triad A-B-C, composed of spin ½ particles A and B and spin 1 particle C (triplet oxygen molecule). Let the initial state of pairs A-B correspond to the fraction of $0<\theta\leq1$ of pairs in the singlet spin state, while the remaining pairs of fractions $(1-\theta)$, as well as all radicals C are equally distributed over all possible states. The initial density matrix of pairs A-B is equal to

$$\rho_0 = \frac{1}{4} - \theta\vec{a}\cdot\vec{b} \tag{S29}$$

Let at each reaction contact in pairs B-C, $1/3$ of the pairs goes into the product and corresponding A-B pairs are removed from those geminate RIPs, which contribute to the recombination fluorescence. Contacts occur at a frequency of f, which is proportional to the concentration of C. Neglecting repetitive encounters with the same particle C, one can obtain that, for sub-ensemble of A-B pairs, in which B have experienced n contacts, the density matrices are

$$\rho_1 = \frac{2}{3}\cdot\frac{1}{4} \quad \rho_2 = \left(\frac{2}{3}\right)^2\cdot\frac{1}{4} \ \dots \ \rho_n = \left(\frac{2}{3}\right)^n\cdot\frac{1}{4} \tag{S30}$$

Here, it is assumed that the spin coherence of the pairs A-B survived after an encounter of B and C completely decays (see Section S3).

Then by the time t, the density matrix of all A-B pairs is the following

$$\rho(t) = e^{-ft}\left(\frac{1}{4} - \theta\widehat{\vec{a},\vec{b}}\right) + \int_0^t d\tau\, e^{-f}\, f\sum_{m=0}^{\infty}\frac{[f(t-\tau)]^m}{m!}e^{-f(t-\tau)}\rho_{m+1} \tag{S31}$$

On the right side of Eq. (S31) the first term refers to pairs, in which the particle B has not contacted with C, the expression $(d\tau\cdot e^{-ft}f)$ is equal to the probability of the first encounter in a time interval $(\tau;\ \tau+d\tau)$, and the sum is to take into account the probabilities to undergo m contacts in the remaining interval $(\tau;\ t)$.

Simplification of Eq. (S31) using (S30) gives the following result

$$\rho(t) = e^{-\frac{1}{3}ft}\left(\frac{1}{4} - e^{-\frac{2}{3}ft}\theta\vec{a}\cdot\vec{b}\right) \tag{S32}$$

The first exponent on the right side of Eq. (S32) describes the monomolecular kinetics of the decay of pairs *A-B* due to the reaction, and the exponent in the parentheses describes the spin relaxation due to spin decoherence within the subensemble of all remaining *A-B* pairs. Eq. (32) shows that the ratio between the characteristic times of the spin decoherence and the reaction rate equals to 0.5. Similar value of the ratio was found in the experiments at fast diffusion (see Figure 2 in the main text).

Let us consider now the case of the absence of the fast paramagnetic relaxation in particle *C*. In this case, spin-selective reaction also results in the spin decoherence in survived pairs *A-B* but in a lesser extent. The density matrix describing the state of the *A-B* pairs after the first contact between *B* and *C* will be described by the density matrix

$$\rho_1 = Tr_c \rho' = \frac{1}{6} - \frac{10}{27} \theta \vec{a} \cdot \vec{b} \tag{S33}$$

The result (S33) is obtained from equation (S23) taking into account the form of the projection operator (S24). Using (S33) as the initial state before the second encounter, we obtain for ρ_2 a result similar to (S33), but with different values of the numerical coefficients on the right side of this expression. For the state of pairs *A-B* when *B* have experienced n encounters with *C*

$$\rho_n = Tr_c \rho' = \frac{1}{4} \left(\frac{2}{3}\right)^n - \left(\frac{10}{27}\right)^n \theta \vec{a} \cdot \vec{b} \tag{S34}$$

Averaging (S34) over the Poisson distribution, we obtain the following expression for the state of the ensemble of pairs at time *t*:

$$\rho(t) = e^{-\frac{1}{3}ft} \left(\frac{1}{4} - e^{-\frac{8}{27}ft} \theta \vec{a} \cdot \vec{b}\right) \tag{S35}$$

It can be seen from Eq. (S35) that in this case, the ratio between the characteristic times of the reaction-induced spin decoherence and the reaction rate equals to 9/8.