Determination of Reactivities of Primary, Secondary, and Tertiary C−H Bonds in Saturated Hydrocarbons from S_2-Xanthione Fluorescence Quenching

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A procedure for determination of reactivity of primary, secondary, and tertiary C−H bonds in molecules of saturated hydrocarbons has been proposed. The procedure involves measurements of picosecond lifetimes of xanthione in the S_2 state (τ_{S2}) from the fluorescence decay (by the TCSPC method) in selected hydrocarbons as solvents. On the basis of the lifetimes measured, the rate constants of hydrogen abstraction, (k_H), are determined for hydrocarbons having only primary C−H bonds, primary and secondary C−H bonds, and primary and tertiary C−H bonds. The obtained highly accurate k_H values show significant differences and are $k_H = 1.4 \times 10^{10}$ s^{-1}, 5×10^{10} s^{-1} and 20×10^{10} s^{-1}, for the primary, secondary, and tertiary bonds. The values of k_H determined by the procedure proposed can be used to assess the relative energy of C−H bonds and to infer about the presence of steric hindrance for the reactive tertiary C−H bonds. They can also be of interest in the studies of primary photochemical processes in hydrocarbon solvents and in the proper choice of solvents for photophysical and photochemical studies.

I. Introduction

Saturated hydrocarbons are most often used as weakly interacting and chemically inert solvents and in this role they have been applied in the spectroscopic and photophysical studies and in investigation of chemical reactions of molecules in the ground state.[1−8] When studying reactive molecules in electronic excited states (S_1, S_2, and in particular T_1), hydrocarbons can take part in their deactivation by reversible or irreversible hydrogen atom abstraction from the C−H bonds.[9−19] This happens in particular for molecules in the T_1 state of relatively high energy and long lifetime, for example in frequently studied T_1-ketones.[9−12] In highly chemically inert perfluorohydrocarbons, their τ_{T1} is particularly long $\sim 10^{-3}$ s,[20] while in hydrocarbons it is significantly shortened to $\sim 10^{-6}$ s, as a result of a very efficient process of hydrogen abstraction from the solvent.[9−12,21] The rate constant of this process (k_H) strongly depends on reactivity of the hydrocarbon used as a solvent and also on the energy and electronic configuration of the T_1 triplet state of the compound studied.[9−12,21] Even for the most reactive hydrocarbons, k_H is much lower than 10^{10} s^{-1}. It usually takes a value from the range 10^5-10^6 s^{-1}, which means that the activation energy of hydrogen abstraction is much greater than zero and the process requires a large number of collisions between T_1-ketone and solvent ($>10^5$ collisions).[22] Although the reactivity of the hydrocarbons used as solvents usually has not been isotropic, as implied by their structure, and different E_{C-H} energies of primary, secondary, and tertiary C−H bonds exist, hitherto, almost the only experimentally observed overall value of k_H has been determined.

Determination of exact values of k_H corresponding to particular orders of C−H bonds can be of great help in interpretation of the phenomena observed. The accurate determination of these values requires a proper choice of the method of measurement including a proper choice of a probe and the solvent. The hitherto performed experiments, in which the reaction mechanism was studied and the yield of product formation determined,[23,24] or in which spectroscopic measurements of quenching of emission from excited triplet states of molecules dissolved in hydrocarbons,[25] have confirmed the fact that the values of E_{C-H} decrease as $E(CH_3) > E(CH_2) > E(CH)$.[26−31] Therefore, it can be expected that the rate constant of hydrogen atom abstraction is the lowest for CH_3 groups and the highest for CH groups. Indeed, the relative values of the rate constants $k_H(I)$, $k_H(III)$,[23,25] and $k_H(II)$[25] increased with increasing C−H bond order, but their ratios (i.e. $k_H(III)/k_H(I)$) were different in these two works even for the same hydrocarbon. The aim of our study was to develop an effective method for determination of reactivity of C−H bonds saturated hydrocarbons.

Correct determination of the rate constants, k_H, of hydrogen abstraction from C−H bonds of different order should bring more information on the mechanism of hydrogen abstraction reactions for hydrocarbons of different structure. The k_H values can also be used for assessment of the relative energy of C−H bonds in hydrocarbons with easy access to C−H bonds and enable us to infer information about the steric hindrance in hydrocarbons with tertiary C−H bonds.

II. The Choice of the Method and the Probe

The choice of a proper method of measurement is of vital importance in determination of the rate constants of the reaction of hydrogen abstraction from different C−H bonds. The purely chemical method, which is based on the observation of the efficiency of formation of stable products as a result of hydrogen abstraction from several hydrocarbons by highly reactive excited probe,[23,24] has a fundamental drawback. This is a formation of intermediates, whose efficiency significantly depends on the environment. Consequently, in this indirect method, the value of $k_H(III)/k_H(I)$ strongly depends on the properties of the solvent

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and can also be affected by different contributions of the reversible reactions and different energy of interactions with the solvent. The values of the ratio k_H(III)/k_H(I), when the hydrocarbons acting as quenchers were dissolved in noninteracting perfluoro-*n*-hexane (PFH) (9.7), were much different from those obtained in the case when hydrocarbons were used only as solvents (5.7). However, it is known that the presence of PFH should not affect the result. It indicates that the actual mechanism of formation of stable products of the reaction of insertion to primary and tertiary C−H bonds is more complex and cannot be used for exact determination of k_H. The application of the process of quenching of excited states of the probe for the determination of k_H for a particular order of C−H bonds on the basis of spectroscopic measurements is definitely more direct and reliable. However, it requires a proper choice of a probe, its excited state, and the environment. The results reported by Giering[25] show that the use of systems in which the probe is quenched by hydrocarbon dissolved in noninteracting solvents can lead to an error in the determination of k_H. The error is related to assessment of the relation between the rate constant of the diffusion needed for a collision of the molecules of the probe and the quencher, k_{diff}, and the rate constant of diffusion separation of the encountered pair k^{-}_{diff}. However, if we still want to use systems of this type we cannot excite the probes to the singlet short-lived ($<10^{-9}$ s) states, as for them, the dynamics of the process of quenching is complex and not yet well recognized.[32,33] Nevertheless, it would be possible to use probes excited to longer-lived singlet or triplet states, and then find the rate constants, k_H, from the Stern−Volmer relation between the excited molecule lifetime and the concentration of the quencher. However, this choice in the probe-quencher-solvent system implies the need to solve the problem of self-quenching of the excited probe by the unexcited molecules of the probe.[13] The incorrectly estimated contribution of this process can lead to incorrect values of k_H.

The reactivity of the excited probe molecule cannot be too high, because each encounter with the quencher molecule would lead to its deactivation at the same rate for all three kinds of C−H bonds. This has taken place when the molecule of S_2-adamantanethione[15,16,34] or the very reactive biradical (:CH_2) has been used.[35]

The aim of our study was to determine the k_H values for C−H bonds formed by primary (CH_3), secondary (CH_2), and tertiary (CH) carbon atoms with the use of a system and method ensuring elimination of all the above-mentioned errors. It was to be achieved by investigation of S_2-xanthione (S_2-XT) fluorescence quenching by hydrocarbons and S_2-XT lifetime τ_{S2} determination by the time correlated single photon counting (TCSPC) technique.[36,37] The choice of S_2-XT as a probe was made to avoid the problems related to self-quenching because of a short lifetime of S_2-XT.[36−39] Thioketones in the S_2-state are highly reactive, which ensures that the process of quenching by hydrocarbons will be the most important path of S_2-XT deactivation, even for the least reactive hydrocarbon containing only primary C−H bonds. On the other hand, the energy of the S_2 state for XT (E_{S2}) is small enough ($E_{S2} \sim 67$ kcal/mol[13,40]) to enable detection of differences in the reactivity of C−H bonds of the lowest energy. The lifetime of S_2-XT determined in these conditions will be very short (∼15−50 ps), but thanks to the use of a very stable TCSPC system[36] and a special procedure for analysis of the results, it will be very accurate.[37]

As shown by the results illustrating the influence of the isotope substitution H/D in the hydrocarbon molecule[41] or in the xanthione (XT) molecule[42] on the τ_{S2} of XT, the mechanism of quenching involves the total or partial abstraction of hydrogen atoms from the hydrocarbon (solvent) molecules. Therefore, the value of k_H is directly related to E_{C-H}. The hydrogen abstraction by S_2-thioketones is reversible. This follows from a comparison of a high value of the quantum yield of the primary process of hydrogen abstraction (indicated by a 10-fold shortening of τ_{S2} when perfluorohydrocarbons used as solvents are replaced by hydrocarbons[13,38,40]) with the low value of the quantum yield of the photochemical decay of XT ($\phi_{XT} < 10^{-2}$).[43,44] This reversibility is a very advantageous feature of thiones,[13,40,45] as it allows accurate determination of τ_{S2} and thus k_H, disregarding the photochemical processes.

The correct choice of solvents-quenchers of a suitable structure would permit a direct and reliable determination of k_H . Determination of the values of k_H for the C−H bonds of the same order for a few different hydrocarbons with a different number of primary and secondary or primary and tertiary C−H bonds should show, if they are similar for different bonds of the same order. The results are expected to prove that the hydrocarbons studied could be used as reference standards to assess the influence of steric hindrances on k_H in other, more complex structures of hydrocarbons. The use of a very stable TCSPC system, an appropriate procedure of picosecond lifetime determination,[36,37] and the HPLC method[46] to check if the emission comes only from the compound studied, ensures a small error of the k_H values obtained.

III. Experimental Section

Xanthione was synthesized as previously described[40,43] and was purified by HPLC. Impurities were present in undetectable amounts and were estimated to be of $<10^{-6}$ M concentration in solutions prepared for experiments. Perfluo-tetradecahydrophenanthrene (from PCR Chemicals) and hydrocarbons (from Merck, Aldrich, Alfa, Wiley) were purified by passing them through a silica gel and alumina column and by fractional distillation. They were free from fluorescent impurities.

UV−visible absorption spectra were recorded on Jasco UV−vis 550 instrument, and emission and excitation spectra were taken on a Perkin-Elmer MPF-3 spectrofluorometer modified with a cooled PMT, single photon counting detection system. Unless otherwise noted, all emission lifetime were made at room temperature using nondegassed solutions.

To obtain reliable values of k_H, we had to determine first the S_2-XT lifetime with the best possible accuracy. To ensure this best possible accuracy, we have applied the HPLC based method of purity control and a very stable system of single photon counting (TCSPC) described in detail in ref 36. In this work, we will just briefly mention that the emission spectrometer employed a laser system Spectra-Physics in the excitation pathway and a single photon counting system in the detecting system. The laser system was composed of a pulse Ti:sapphire laser Tsunami (720−1000 nm, 82 MHz, 1 W, 1−2 ps) pumped by an argon ion laser BeamLok 2060 (10 W), a pulse selector employed to decrease the pulse frequency to 4 kHz, and a generator of the second and third harmonics. The exciting beam of the vertical polarization was applied to excite the fluorescence collected at the magic angle. The shape of the laser pulses was controlled by an autocorrelator. For detection of photons, we used a fast photomultiplier MCP−PMT R3809U-05 (Hamamatsu). The FWHM of the instrument response function (IRF) was 35 ps. The data were collected from 1024 channels with a time resolution MCA of 0.61 ps/channel. The measurements were performed using the reference method,[37] and the results were analyzed by a homemade software which allowed the use of the Levenberg−Marquardt or Simplex optimization algorithms.[47] To eliminate the IRF dependence on the emission and excitation wavelength, the delta-function convolution method (DFCM) was used.[48]

IV. Determination of the k_H Rate Constant

In general, the lifetime of S_2-XT dissolved in a saturated hydrocarbon can be expressed as:

$$\tau_{S2} = \frac{1}{k_F + k_I + k_H}, \tag{1}$$

where k_F is the fluorescence rate constant, k_I the radiationless intramolecular deactivation rate constant, and k_H the rate constant of quenching by the hydrocarbon. In the case of hydrocarbon solvents, which relative to highly reactive S_2-thioketones are effective quenchers, the k_H rate constant is a time-independent quantity but it depends on the number and kind of C−H bonds in the hydrocarbon. Assuming the same probability of the quenching process between each C−H bond of a given order, and the excited S_2-XT molecule, the average k_H value can be expressed as:

$$k_H = \frac{A}{N}k_H(I) + \frac{B}{N}k_H(II) + \frac{C}{N}k_H(III) \tag{2}$$

where N is the number of all C−H bonds in a given hydrocarbon, A, B, and C are the numbers of primary, secondary, and tertiary bonds, and k_H(I), k_H(II), and k_H(III) are the rate constants of quenching by the primary, secondary, and tertiary C−H bonds.

The values of all k_H(I), k_H(II), and k_H(III) rate constants were obtained by determination of the rate constants k_F and k_I, followed by determination of k_H(I), k_H(II), and k_H(III). The values of k_F and k_I rate constants were obtained from the measurements of S_2-XT lifetime and fluorescence quantum yield ($\Phi_F = 1{,}3 \times 10^{-2}$) in perfluorotetradecahydrophenanthrene (PF), which is a perfluorohydrocarbon whose interactions were the closest to those in the hydrocarbons used.[49] Because of the weak interactions and chemical inertness of perfluorohydrocarbons, the S_2-XT dissolved in them undergoes only intramolecular—radiative and radiationless deactivation.[14] The value of τ_{S2} measured for XT in PF is $\tau_{S2} = 148$ ps, so

$$k_{PF} = \frac{1}{\tau_{S2}(PF)} = 6.7 \times 10^9\ s^{-1} \tag{3}$$

The value of k_{PF} is a sum of $k_F = 1 \times 10^8\ s^{-1}$ and $k_I = 6.6 \times 10^9\ s^{-1}$. A replacement of PF by saturated hydrocarbons does not affect the value of k_F[14,40] and has only a slight effect on the value of the XT $\Delta E(S_2-S_1)$ energy gap. Therefore, it can be assumed that the intramolecular radiationless deactivation (k_I) and the fluorescence process (k_F) occur at the same rate in PF and the hydrocarbons used. Since $k_H \gg k_{PF}$, (for the primary C−H bonds, $k_H(I) \geq 2k_{PF}$) the k_{PF} rate constant can be successfully used for determination of the rate constants k_H in hydrocarbons.

V. Results

The Rate Constant k_H(I). On the basis of the above determined k_{PF} value and eq 2, the value of k_H(I) was found [Table 1]. To do that, XT ($c < 1 \times 10^{-5}$ M) was dissolved in two hydrocarbons with only primary carbon atoms. The first one was 2,2-dimethylpropane (neopentane, NP), while the second was a (1:1) mixture of NP and 2,2,3,3-tetramethylbutane (TEMB), which is a solid. The S_2-XT fluorescence decays measured in the two solvents were of monoexponential character (Figure 1). Although TEMB and NP significantly differ in the structure and number of primary carbon atoms, the τ_{S2} lifetimes determined in them are similar. This result proves that the reactivity of a primary C−H bond in these hydrocarbons is not affected (or is very weakly affected) by the properties other than the C−H bond energy, so from the point of view of the quenching process, each of these bonds is of the same significance. Therefore, these hydrocarbons can be treated as solvents characterized by isotropic reactivity. It may seem obvious for NP (a fully symmetric molecule) however, it was not so for TEMB.

TABLE 1: The Measured S_2-XT Lifetime and the Calculated k_H(I) Quenching Rate Constant[a]

solvent	τ_{S2} [ps]	number of bonds I	II	III	$k_H(I) \times 10^{10}$ [s^{-1}]
2,2-dimethylpropane (neopentane)	49.3	12	0	0	1.35
neopentane−2,2,3,3-tetramethylbutane (1:1)	47.2	18	0	0	1.44

[a] The above presented k_H(I) values should be treated as very accurate, which is essential for the claim of reliability of the rate constants k_H(II) and k_H(III).

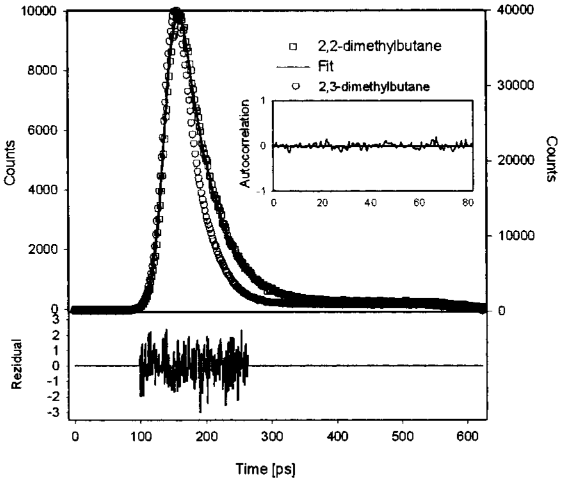

Figure 1. The S_2-fluorescence decay of XT in 2,2-dimethylbutane at room temperature ($\lambda_{exc} = 424$ nm, $\lambda_{em} = 460$ nm, 0.61 ps/channel). The reference fluorescence decay (circles) is that of XT in 2,3-dimethylbutane measured in identical experimental conditions. Squares are experimental data. The best fit is shown as a solid line. Also, the plots of weighted residuals and weighted autocorrelation function are included.

The Rate Constants k_H(II) and k_H(III). To obtain the values of k_H(II) and k_H(III), the decay time of S_2-XT fluorescence was measured in several selected hydrocarbons. The solvents used for measurements of k_H(II) had exclusively primary and secondary carbon atoms, while those used for measurements of k_H(III) had exclusively primary and tertiary carbon atoms, which ensured the simplest interpretation of results. Indeed, as follows from analysis of the structural models of the hydrocarbons, all hydrogen atoms are equally and easily accessible.

Because of a similar linear structure, the same number of primary bonds and a gradually increasing number of secondary bonds, the solvents: pentane, hexane, and decane were selected for k_H(II) determination. The measurements in these solvents were expected to answer the following question: does the mean k_H(II) rate constant depend only on the number of the secondary C−H bonds—as indicated by eq 2—or on other properties (like its polarizability and anisotropy) as well? To check the influence

TABLE 2: The Measured S_2-XT Lifetimes and the Calculated k_H(II) Quenching Rate Constants

solvent	τ_{S2} [ps]	number of bonds I	II	III	k_H(II) $\times 10^{10}$ [s^{-1}]	ratio of bonds of different order
pentane	25.9	6	6	0	4.9	1:1:0
hexane	24.0	6	8	0	5.0	1:1.3:0
decane	20.8	6	16	0	5.1	1:2.7:0
3,3 -diethylpentane	28.1	12	8	0	5.2	1:0.75:0

TABLE 3: The Measured S_2-XT Lifetimes and the Calculated k_H(III) Quenching Rate Constants

solvent	τ_{S2} [ps]	number of bonds I	II	III	k_H(III) $\times 10^{11}$ [s^{-1}]	ratio of bonds of different order
2,3-dimethylbutane	21.7	12	0	2	1.9	6:0:1
2,2,3-trimethylbutane	28.0	15	0	1	2.6	15:0:1

of the molecule structure on the mean value of k_H(II), measurements were also performed in 3,3-diethylpentane—a branched hydrocarbon of spherical symmetry, containing only primary and secondary carbon atoms. The results of the measurements are shown in Table 2. The values of k_H(II) were obtained from eq 2 with the use of k_{PF} and mean k_H(I) values.

With increasing numbers of the secondary carbon atoms forming C−H bonds (CH_2 groups) in the linear hydrocarbon molecule, their contribution in the process of S_2-XT deactivation increases. It is manifested by a well-evidenced decrease in τ_{S2}, in agreement with the results of ref 38. A constant value of k_H(II) for these three hydrocarbons implies that the different contribution of the secondary C−H bonds is the only reason for the difference in τ_{S2} values. The same τ_{S2} in pentane and 3,3-diethylpentane at the same ratio of the secondary to primary carbon atoms suggests the same probability of participation of each bond in the quenching process. On the other hand, the differences in their structure and anisotropy of their properties do not affect the reactivity of the C−H bonds. On the basis of the obtained values of k_H(II), equal reactivity of all the secondary bonds can be assumed.

The value of the k_H(III) rate constant was determined from τ_{S2} measurements for S_2-XT in 2,3-dimethylbutane and 2,2,3-trimethylbutane. Both solvents have only primary and tertiary bonds, however, at different relative contributions. Because they are butane derivatives, they do not differ much in their other properties.

The lifetime values obtained illustrate a significant difference in reactivity between the primary and tertiary bonds. Replacement of the methyl group by a tertiary C−H bond results in a significant shortening of τ_{S2}, which is illustrated by the results for 2,2,3-trimethylbutane (τ_{S2} = 28 ps) and 2,2,3,3,-tetramethylbutane (τ_{S2} = 47 ps). Although an increase in the contribution of tertiary C−H bonds in the molecule of 2,3-dimethylbutane brings a further decrease in τ_{S2}, the value of k_H(III) determined for these hydrocarbons is clearly lower than that for 2,3,3-trimethylbutane.

A comparison of S_2-XT lifetimes in 2,3-dimethylbutane (τ_{S2} = 21.7 ps) and in 2,2-dimethylbutane (τ_{S2} = 35.9 ps) illustrates the difference in reactivity between the secondary and tertiary C−H bonds. In the two solvents of similar physical properties (including interactions), there are 12 primary C−H bonds and 2 tertiary C−H bonds or secondary C−H bonds in 2,3-dimethylbutane and 2,2-dimethylbutane, respectively. The value of k_H(II) calculated for the 2 C−H bonds in 2,2-dimethylbutane is 6.5×10^{10} s^{-1}.

TABLE 4: The Influence of the Error in Determination of τ_{S2} on the Quenching k_H Rate Constant for Primary, Secondary, and Tertiary C−H Bonds

solvent	τ_{S2} [ps]	$\Delta\tau_{S2}$ [ps]	k_H [s^{-1}]	Δk_H [s^{-1}]
neopentane k_H(I)	49.3	-1^a	1.29×10^{10}	-0.04×10^{10}
		$+1^a$		$+0.04 \times 10^{10}$
		-2		-0.09×10^{10}
		$+2$		$+0.08 \times 10^{10}$
		-3		-0.13×10^{10}
		$+3$		$+0.12 \times 10^{10}$
pentane k_H(II)	25.9	-1^a	4.9×10^{10}	-0.31×10^{10}
		$+1^a$		$+0.29 \times 10^{10}$
		-2		-0.65×10^{10}
		$+2$		$+0.56 \times 10^{10}$
		-3		-1.01×10^{10}
		$+3$		$+0.80 \times 10^{10}$
2,3-dimethylbutane k_H(III)	21.7	-1^a	1.9×10^{11}	-0.16×10^{11}
		$+1^a$		$+0.14 \times 10^{11}$
		-2		-0.33×10^{11}
		$+2$		$+0.27 \times 10^{11}$
		-3		-0.52×10^{11}
		$+3$		$+0.39 \times 10^{11}$

[a] τ_{S2} obtained accuracy.

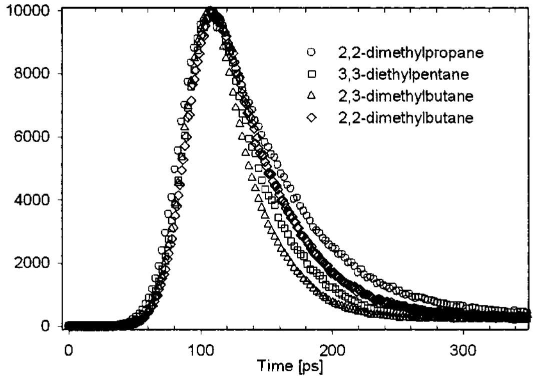

Figure 2. The S_2-fluorescence decay of XT in 2,2-dimethylpropane (τ = 49.3 ps), 3,3-diethylpentane (τ = 28.1 ps), 2,3-dimethylbutane (τ = 21.7 ps), and 2,2-dimethylbutane (τ = 35.9 ps) measured at room temperature (λ_{exc} = 424 nm, λ_{em} = 460 nm, 0.61 ps/channel).

The influence of the error in the determination of lifetimes τ_{S2} on the k_H values is illustrated in Table 4. It should be emphasized that although the values of τ_{S2} are very short, the errors in their determination are very small, which was possible to achieve because of the high stability of the TCSPC system used and a special procedure of measurements and their analysis.[36,37] It should be also noted that the same errors in lifetimes (different in percent) do not give the same errors in the rate constants determined.

VI. Discussion

Analysis of the obtained k_H values should be performed taking into account a few important conditions. First of all, accurate and reproducible measurements of lifetimes in the range 20−50 ps were possible thanks to the time-resolution of the system (0.61 ps/channel), the available methods of lifetime determination, and exceptionally stable work of the TCSPC system used.[36,37] The possibility of determination of τ_{S2} with a very small error ($\leq \pm 1$ ps) was essential, as shown in Figure 2. As a consequence, the obtained values of k_H(I), k_H(II), and k_H(III) are fully reliable.

As follows from the above presented results, the differences between the rate constants k_H(I), k_H(II), and k_H(III) are very significant. This observation is in qualitative agreement with the earlier obtained relative values in refs 23 and 25, and with the estimated relations between the energies of the primary, secondary, and tertiary bonds.[26−31] The quantitative results differ significantly from those reported in refs 23 and 25, which seems to be a result of the fact that these authors had used too complex procedures of k_H determination in which some of the assumptions could not be satisfied.

For the sake of illustration, the accurate values of the bonds energy are $E = 420 \pm 2.5$ kJ for C−H(I) in *n*-propane, $E = 412.5 \pm 1.6$ kJ for C−H(II) in *n*-propane, $E = 410.5 \pm 2.1$ kJ in *n*-butane, and $E = 404.0 \pm 6.3$ kJ for C−H(III) in 2-methylbutane.[26,27] Taking into regard significant differences in k_H for primary, secondary, and tertiary C−H bonds, irrespective of the hydrocarbon used as a quencher of S_2-XT fluorescence, it can be concluded that, as expected, the relative relations $k_H(I):k_H(II):k_H(III)$ are determined by the energy of the bonds $E_{C-H}(I) > E_{C-H}(II) > E_{C-H}(III)$, which depends on the closest neighborhood. Relatively small differences in k_H for primary and secondary C−H bonds obtained for different hydrocarbons (e.g. pentane and decane) can be explained by a small error in determination of τ_{S2}. However, significantly higher k_H for 2,2,3-trimethylbutane than for 2,3 dimethylbutane for tertiary bonds, slightly higher $k_H(I)$ for 2,2,3,3-tetramethylbutane than for neopentane for primary bonds and the relations: k_H(decane) > k_H(hexane) > k_H(pentane) for secondary bonds can be a result of a greater number of C atoms (electronegativity 2.5) than H atoms (electronegativity 2.1) in a farther vicinity of the C−H bond considered. Nevertheless, a similar value of $k_H(II)$ obtained for pentane and decane indicates that the energy of C−H bonds in all CH_2 groups is very similar irrespective of their position in the hydrocarbon chain. This is a very important conclusion in the aspect of the controversies about this subject[29,50] and the difficulties in accurate measurement of energy of different C−H bonds.[26,27] The results show that the significant decrease in the energy of the secondary C−H bonds in subsequent methylene groups in the alkane chain is not correct. However, it cannot be excluded that small differences in the $k_H(II)$ values obtained for linear hydrocarbons (i.e. slightly higher $k_H(II)$ for decane than for pentane) are due to somewhat smaller reactivity of the C−H bonds in CH_2 groups in direct neighborhood of the terminal CH_3 groups. The greater the number of H atoms than C atoms present near the C−H bond considered, the greater the energy of the bond and thus the smaller the k_H value. A significantly higher $k_H(III)$ for 2,2,3-trimethylbutane than for 2,3-dimethylbutane (Table 3) supports this conclusion. This observation is indirectly supported by a significantly higher $k_H(II)$ for 2,2-dimethylbutane ($k_H(II) = 6.5 \times 10^{10}$ s^{-1}) than for all other hydrocarbons studied. These results indicate that the energy of the C−H bond and thus its k_H value is affected not only by the nearest neighborhood of this bond, although it depends mainly on its order.

The results obtained have shown that S_2-XT is a very good probe for determination of reactivity of different C−H bonds in hydrocarbon molecules. It is reactive enough to ensure that the process of quenching is relatively efficient even in the case of interaction with the least-active primary C−H bonds. Consequently, the contribution of the process can be accurately determined. On the other hand, although the process of quenching by the most reactive tertiary bonds runs at a very high rate constant, there still is the energy barrier for hydrogen abstraction from hydrocarbon molecules, i.e., the activation energy for this process is small but greater than zero. Therefore, for practically all C−H bonds in saturated hydrocarbon molecules, the values of k_H and E_{C-H} are directly related. Owing to this, the measurement of the time-resolved emission decay is directly related to the S_2-XT fluorescence quenching in the process of total or partial, mostly reversible ($\Phi_{XT} < 10^{-2}$)[38,40−45] hydrogen abstraction from the hydrocarbon molecule, and τ_{S2} is directly related to k_H. Thanks to the very high reactivity of the thiocarbonyl group in the S_2 state, the hydrogen abstraction from the hydrocarbon molecules of different reactivity and structure runs at a rate constant $k_H \sim 10^{10}-10^{11}$ s^{-1}. In these conditions, τ_{S2} is long enough to be measured accurately using the procedure described in ref 37, and simultaneously short enough for the intramolecular deactivation processes competitive to hydrogen abstraction not to have a great influence on τ_{S2} and the influence of secondary processes on the S_2-XT fluorescence to be negligible.

VII. Conclusions

The above-described method for determination of the reactivity of the C−H bonds of different orders enables us to obtain reliable values of k_H for different structure hydrocarbons. The advantages of the method can be summarized as follows:

There is a simple relationship between the τ_{S2} value and the reactivity (k_H) of the C−H bonds.

The accurate and reproducible measurement of τ_{S2} (from the range 5−50 ps) by TCSPC method ensures accurate determination of k_H (Table 4).

A very high yield of S_2-XT quenching by hydrocarbons used as solvents, $k_H \geq 10^{10}$ s^{-1} and monoexponential character of S_2-XT fluorescence decay, ensure the universal character of this method.

No secondary processes (including photochemical ones) affect the k_H values determined.

It is not important whether the quenching leads to formation of radicals (as a result of total homolitic cleavage of C−H bonds) or radical-like individuals.

Fluorescence comes exclusively from S_2-XT, since the radicals or radical-like individuals do not emit radiation.

A high value of k_F ($\sim 10^8$ s^{-1}) for the transition $S_0 \rightarrow S_2$, despite a short τ_{S2}, ensures that the intensity of XT fluorescence in hydrocarbons is sufficiently high ($\Phi_F \geq 10^{-3}$).

The concentration of XT is low enough ($\leq 10^{-5}$ M) to guarantee the presence of only monomer molecules in the solution.

The long wavelength excitation ($\lambda_{exc} = 370-430$ nm) should ensure exclusive excitation of ($S_0 \rightarrow S_2$) XT; in these conditions the emission from hydrocarbon impurities has practically no effect on the measured S_2-XT decay.

Great photochemical and thermal stability of XT permits multiple measurements of S_2-XT fluorescence decay for samples of low volume and minute amounts of the photoproducts formed have no influence on the value of τ_{S2} determined.

The large differences in k_H determined for primary, secondary, and tertiary C−H bonds indicate great anisotropy of reactivity of the majority of hydrocarbon molecules. The hitherto obtained k_H values are usually the overall values, depending mainly on the number of C−H bonds of a given order. They show that a comparison of hydrocarbons with one another and with other classes of solvents should be made with great care. Also, the choice of a proper hydrocarbon as a solvent in photophysical and photochemical studies must be very careful. A good illustration of this point is the great difference in τ_{S2} obtained for S_2-XT in 2,3-dimethylbutane and 2,2-dimethylbutane, which seemingly are very similar solvents.

Although the reliability and accuracy of determination of the C−H bond energies in small and simple molecules of hydrocarbons are high,[26,27] these energies cannot be found for larger molecules of more complex hydrocarbons. Taking into regard the correctness of the procedure of k_H determination proposed in this work and a direct relationship between E_{C-H} and k_H, the obtained k_H values can be used to assess the relative energy of C−H bonds for the molecules of such hydrocarbons and to find out in which hydrocarbons the access to the C−H bonds is not easy.

Apart from E_{C-H}, another factor influencing the rate constant value is the accessibility to the H atom from a given bond. If the access to a reactive bond is obstructed, the probability of quenching process decreases, which affects the values of k_H. Because the mechanism of S_2-XT quenching by hydrocarbons requires a direct contact between the molecules of these two compounds, it will be possible to determine the influence of steric hindrances on the value of k_H by using the method proposed. It will be particularly valuable for highly reactive tertiary C−H bonds, which are few in number and may be hardly accessible.

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