Oxygen quenching of excited singlet and triplet states of polycyclic aromatic hydrocarbons in the vapor phase

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ABSTRACT

In vapor-phase oxygen quenching rate constants of excited singlet (k_S^{O2}) and triplet (k_T^{O2}) states were investigated for polycyclic aromatic hydrocarbons having significantly distinguishing oxidation potentials E_{ox}. The significant spread in the rate constants was found ($4 \cdot 10^5$ s^{-1} torr^{-1} < k_S^{O2} < $1.2 \cdot 10^7$ s^{-1} torr^{-1}; $5 \cdot 10^2$ < k_T^{O2} < $4 \cdot 10^5$ s^{-1} torr^{-1}). The values of both k_S^{O2} and k_T^{O2} change linearly in the logarithmic scale with free energy change for complete electron transfer ΔG_{ET}, which points that the charge transfer interactions are involved in the oxygen quenching of the S_1 and T_1 states in vapor-phase. © 2008 Trade Science Inc. - INDIA

KEYWORDS

1. INTRODUCTION

The polycyclic aromatic hydrocarbons (PANs) are compounds that are of interest from the environmental standpoint. They are frequently released into atmosphere from the industrial wastes and the petroleum spills and play important role in atmospheric photochemistry. Their natural photochemical oxidation and singlet oxygen mediated processes in the atmosphere have attracted attention as possible decontamination way[1]. The most significant success was achieved in the understanding of the interactions of organic molecules with O_2 in solutions. To date, there are only several works devoted to the study of such interactions of polyatomic molecules in vapor phase[2]. However, experimental data obtained for the gas phase serve as the basis for verification of modern theoretical models and provide necessary information for modeling gas-phase photochemical processes. Moreover, in the gas phase, where the effects caused by solvent and molecular diffusion are absent, the dependences of the oxygen quenching rate constants on individual properties of interacting molecules can be determined uniquely.

At the present work, the oxygen quenching rate constants of excited singlet S_1 (k_S^{O2}) and triplet T_1 (k_T^{O2}) states were estimated in vapor-phase for PANs: anthracene (A), 9-methylanthracene (9-MA), 9-nitroanthracene (9-NA), 9,10- dibromoanthracene (9, 10-DBA), 2-aminoanthracene (2-AA), and 9,10-dicyanoanthracene (9,10-DCA), chrysene (Chr), phenanthrene (Phen), fluoranthene (Fl) and carbazole (Car) having significantly distinguishing oxidation potentials E_{ox}. (0.44 V < E_{ox} < 1.89 V vs SCE).

2. EXPERIMENTAL

Nitrogen lasers generating pulses with a half-width of 1.5 ns or 100 ps, energy of 2 mJ or 50 μJ, and

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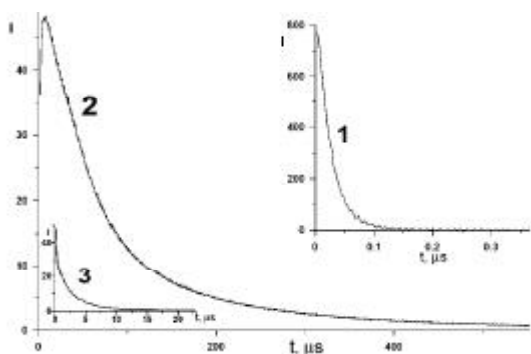**Figure 1: The time-resolved emission of 2-AA at vapor pressure 0.46 Torr, T=423 K, λ_{obs}=417 nm: fast component (1), slow components (2) and (3) at P_{O2}=0 and 1.32 Torr, respectively**

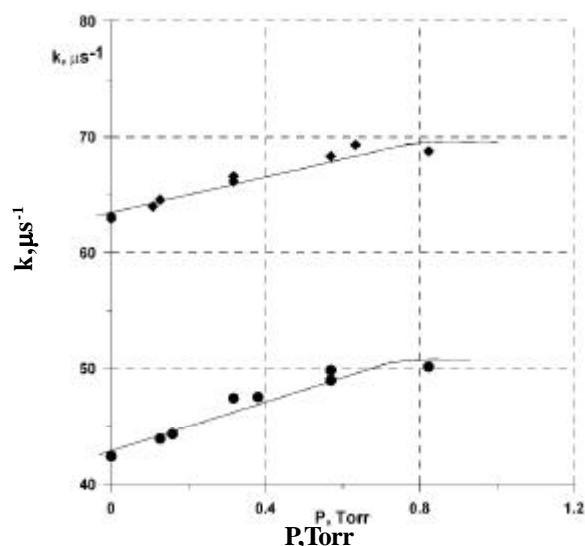**Figure 2: Plot of the 2-AA decay rates k_S vs P_{O2} at different temperature of vapors: •-473 K, ♦ -453 K**

repetition rate of 10 Hz were used for excitation. The measurements at different wavelengths were carried out with the interference filters with transmission band of half-width 1.5-2 nm. The spectra were recorded on a scanning monochromator. Time-resolved luminescence was measured using a system consisting of photomultipliers: Hamamatsu R1828-01 or FEU-79 and Tektronics digital oscilloscope (TDS 3032B 300 MHz) connected to an IPM PC. A dual channel signal acquisition was used. In each measurement, as much as 500 signals were detected and analyzed by least-squared fitting method with a personal computer. Samples were prepared in a vacuum quartz cell heated to a required temperature (423-623 K). The cell was connected to a vacuum system via dry valve and evacuated to 10^{-6} torr. Oxygen was added to the cell via dry valve from a

glass reservoir.

The laser-induced luminescence of PANs has a fast and slow component (**Figure** 1). The fast nanosecond component corresponds to fluorescence from the first singlet state S_1 with decay times changing from 8 ns to 28 ns. In addition, PANs emit a delayed fluorescence (DF) due to the bimolecular annihilation of two triplet molecules. A rapid intersystem crossing $S_1 \rightarrow T_1$ was exploited to prepare sensitizer molecules in a triplet state. The initial part of the DF curves, which does not exceed several microseconds after the excitation, is described by hyperbolic function ($I^{-1/2}$= at + b), but DF decay curves within the range from 100μs after the excitation to $2\tau_T$ where τ_T is the decay time of the triplet state, are well approximated by an exponential curve. This long component was used for estimation of the oxygen quenching rate constants of the triplet states. Both the fast and slow component decay rates as well as the relative intensities of fluorescence and DF are measured in the temperature range 423-623 K for mixtures of PANs vapors with oxygen.

PANs were purchased from Aldrich. In addition, substances were purified by sublimation.

3. **RESULTS**

(I) The decay rates k_S of the fluorescence at $0 < P_{O2} <$ 2-20 torr and decay rates k_T of DF at $0 < P_{O2} < 5$-20 torr increase linearly with increasing oxygen pressure: $k_S = k_{01} + k_S^{O2} \cdot P_{O2}$ and $k_T = k_{02} + k_T^{O2} \cdot P_{O2}$, where k_{01}, k_{02} are the decay rates of the fluorescence and DF, respectively, in the absence of the oxygen, k_S^{O2} and k_T^{O2} are the quenching rate constants of the states S_1 and T_1. At higher pressure, the behavior of the dependences $k_S (P_{O2})$ and $k_T (P_{O2})$ become nonlinear (Figure 2). The k_S^{O2} and k_T^{O2} were estimated by the linear portion of the dependences $k_{S(T)} (P_{O2})$, and the quenching efficiencies were calculated as $\beta = k_{S(T)}^{O2}/k_{gk}$ (k_{gk} is the rate constant of gas-kinetic collisions, the value of which was calculated with radii of PANs taken from[3] and r_{O2}=2 Å.

(II) A decrease in the time–integrated fluorescence intensity I_1 and DF intensity I_2 with P_{O2} increase was detected. The dependences (I_1/I_{01}) (P_{O2}) and I_2/I_{02} (P_{O2}) (I_{01}, I_{02} and I_1, I_2 are the time integrated
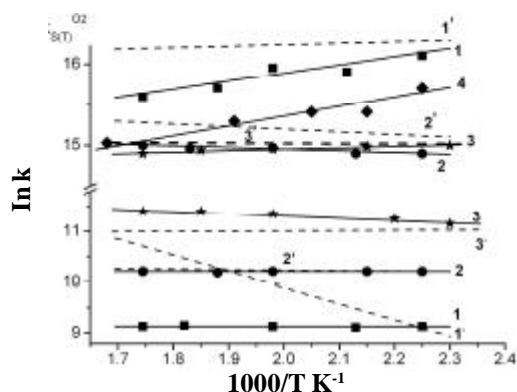
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Figure 3: Plot of the DF relative intensities I/I$_0$ of 9-MA vs. P$_{O2}$ at different temperature of vapors

intensities in the absence and presence of oxygen, respectively) are level off with P$_{O2}$ increasing. By the values of (I$_{01}$/ I$_1$) and (I$_{02}$/ I$_2$), corresponding to the saturation of the dependences (I$_{01}$/ I$_1$) (P$_{O2}$) and (I$_{02}$/ I$_2$) (P$_{O2}$), we estimated the fraction of the oxygen-quenched singlet (q$_S^{O2}$=1- I$_1$/ I$_0$) and triplet (q$_T^{O2}$ = 1- I$_2$/ I$_{02}$) states.

(III) In the temperature range 423-623 K the oxygen quenching rate constants either do not change with temperature growth or show weak negative temperature dependence in the PAN vapors (Figure 3).

(IV) In the gas phase, new luminescence bands did not appear under conditions of experiment.

4. DISCUSSION

In solutions the oxygen quenching of excited states of aromatic hydrocarbons, including PANs, has been a subject of several investigations[2-8]. In the case of the quenching of the state S$_1$, oxygen can be formed either in one of the singlet states or in the ground triplet state. If the energy gap ΔE$_{ST}$ between the S$_1$ and T$_1$ exceeds the energy E$_?$ of the level $^1\Delta_g$ of O$_2$, direct energy transfer from S$_1$ to O$_2$ can occur with formation of singlet oxygen ^{1}O$_2$. The oxygen-enhanced intersystem crossing (ISC) S$_1$→T$_1$ with the formation of O$_2$ in the ground triplet state is frequently considered as the most important process for deactivation of the S$_1$ in solutions. However, this case is far from being general. Other observations have also been reported for aromatic hydrocarbons in solutions[4,8].

The oxygen quenching of the triplet states T$_1$ sug-

gests: (i) electronic energy transfer from the sensitizer to oxygen, followed in the majority of solutions with a high (up to 100%) efficiency of ^{1}O$_2$ formation, and (ii) the oxygen-enhanced ISC T$_1$→S$_0$, considering as the most probable process in solutions.

The most important features of the PANs being investigated are as follows: (I) for all the PANs, except for chrysene, carbazole and phenanthrene, the energy gap (ΔE$_{ST}$) exceeds the energy of the first singlet level of oxygen, equal to 7882cm^{-1} (ΔE$_{ST}$>ΔE$_\Delta$=7882cm^{-1}). Therefore, for most PANs make it possible to produce singlet oxygen due to energy transfer from both the singlet and triplet molecules, (II) the close-to-unity sum of quantum yields of the fluorescence and of the triplet formation due to the intersystem crossing (ISC) S$_1$→T$_1$. The effect of rate of the internal conversion (IC) S$_1$→S$_0$ on the k$_S$ of PANs is negligibly small in vapors and neutral media. Therefore, the state S$_1$ PANs can be quenched by O$_2$ via two channels: the formation of singlet oxygen and triplet molecules of PANs due to energy transfer (with a rate constant k$_?$); the formation of triplet molecules of both reagents due to oxygen-enhanced ISC S$_1$→T$_1$ (with a rate constant k$_{ST}$). In this approximation, the rate constant of k$_S^{O2}$ was determined in[9]

$$k_S^{O2}= [k_{col}(k_{ST}+ k_\Delta)]/(k_{-col}+ k_\Delta + k_{ST}) \qquad (1)$$

where k$_{col}$ and k$_{-col}$ are the rate of gas–kinetic collisions and collision complex dissociation.

The triplet T$_1$ levels of PANs, located above the singlet levels of O$_2$ can be quenched by O$_2$ via both the electronic energy transfer (with a rate constant k$_{et}$) and the oxygen-enhanced ISC T$_1$→S$_0$ (with a rate constant k$_{TS0}$). So in the gas phase, the k$_T^{O2}$ was determined in[10] as

$$k_T^{O2}=1/9 \ k_{col}k_{et}/(k_{-col}+k_{et})+1/3k_{col}/(k_{-col}+k_{TS0}) \qquad (2)$$

For the easily oxidized sensitizer molecules, in solutions and even in the vapor-phase, the decay rates of k$_S$ and k$_T$ are affected by the charge-transfer (CT) interactions leading to the formation of excited complexes of different multiplicity, ^{3}(S$_1$O^2)*, ^{1,3,5}(T$_1$O^2)*, some of which are stabilized by CT from PANs molecules to the oxygen[2,8,9,10].

As follows from (1), for several PANs (A, 9MA, 2AA) the rather high initial values of ISC rate (k$_{ST}$≅2·10^8 s^{-1}) that were enhanced in addition due to CT interac-

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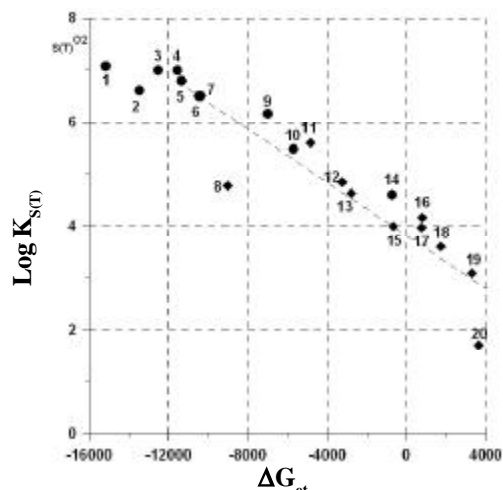**Figure 4: Plot showing the dependence of log k_S^{O2} and log k_T^{O2} for series of ANTs on the free energy change for full electron transfer ΔG_{et}. The insert shows the correlation of E_{ox} vs I_p**

TABLE 1: Experimental values of the quenching rate constants of singlet (k_S^{O2}) and triplet (k_T^{O2}) states; fractions of the oxygen quenched singlet (q_S^{O2}) and triplet (q_T^{O2}) states for PANs in vapor-phase at T=423 K

Compounds	E_s, cm^{-1}	$k_S^{O2}/10^7$ s^{-1} torr^{-1}	q_S^{O2}	ΔG_{et}, cm^{-1}
2-Aminoanthracene	24990	1,20	0,54	-15160
Anthracene	28100	1,20	0,72	-12536
9-Methylanthracene	25600	1,20	0,50	-11568
Carbazole	28950	0.70	0.65	-13463
Phenanthrene	28900	0.33	0.38	-10370
Chrysene	27640	0.30	0.75	-10463
9,10-Dibromoanthracene	24800	0,15	0,40	-7616
9,10-Dicyanoanthracene	23300	0,04	0,01	-786

Compounds	E_t, cm^{-1}	$k_T^{O2}/10^4$ s^{-1} torr^{-1}	q_T^{O2}	ΔG_{et}, cm^{-1}
2-Aminoanthracene	14600	40,00	0,98	-4800
Phenanthrene	21640	7.00	0.98	-10370
Chrysene	19980	2.77	0.80	-2801
9-Methylanthracene	14700	1,00	0,86	-429
Fluoranthene	18475	3.00	0.94	799
Anthracene	14880	0,93	0,93	764
9-Nitroanthracene	14630	0,40	0,74	1741
9,10-Dicyanoanthracene	13300	0,05	0,12	3630
9,10-Dibromoanthracene	14060	0,30	0,30	3940

tions, exceed the values k_{col} at P_{O2} used. In such a case the highest quenching rates approach the gas kinetic ones. Therefore, the dependences of k_S^{O2} on the electron-donor characteristics, in particular, on the gas-phase ionization potentials I_p were not detected. Moreover, under condition $k_{ST} > k_A$, it is assumed no production of singlet oxygen. For others PANs the decrease of rate constant values from the largest k_S^{O2} to the smallest k_T^{O2} by four orders of magnitude corresponds to increase in E_{ox} from 0.44 to 1.89 V vs SCE.

The dependences of k_S^{O2} and k_T^{O2} on the free energy change of complete electron transfer ΔG_{et}, estimated by Rehm-Weller equation[11]:

$$\Delta Get = F(E_{ox} - E_{red}) - E_{S1(T1)} \qquad (3)$$

where F is the Faraday constant, are shown in figure 4. The E_{ox}, obtained in neutral solutions (E_{ox}=1.89; 1.61; 1.53; 1.45; 1.35; 1.21; 1.20; 1.14; 0.96; 0.44 V via SCE for 9,10-DCA[12], Fl[14]; Phen[14], 9,10-DBA[13], Chr[14]; 9-NA[13,14], Car[13]; A[13,14], 9-MA[13,15], 2-AA[14], respectively), and the oxygen reduction potential E_{red} = -0.78 V via SCE were used. The liner correlation between E_{ox} values used and the gas-phase I_p was found. In the region –11000 cm^{-1}<ΔG_{et}<4000 cm^{-1}, a general dependence, close to linear for the whole set of log $k_{S(T)}^{O2}$ was obtained. This dependence shows the increase of the $k_{S(T)}^{O2}$ with ΔG_{et} decrease. By the linear dependence log $k_{S(T)}^{O2}$ on ΔG_{et}, we estimated the degree of electron transfer δ which was found to be small (δ=18 %) with respect to the complete electron transfer (the expected slope -(2.3 kT)$^{-1}$[11]) as for some other polycyclic aromatic compounds in non-polar solvents[16,17]. Good linear correlation between log($k_{S(T)}^{O2}$) and ΔG_{et} suggests the involvement of CT interaction in the oxygen quenching of PANs excited states. It is the indication that quenching of the states S_1 and T_1 by O_2 can proceed by the mechanism involving the formation of CT complexes (PAN$^{\delta+}$O2$^{\delta-}$) with the same partial CT character. As follows from the data of the TABLE 1 the fraction (q_S^{O2}) and (q_T^{O2}) of the quenched singlet and triplet states depend on ΔG_{et}, confirming that in the vapor phase the oxygen quenching can be governed by CT interactions and that the singlet and triplet states of PANs vapors are quenched incompletely by O_2.

In contrast to the widely used opinion that the quenching in the gas phase is controlled by collisions, the quenching efficiencies of the state S_1 of PANs were found to be either comparable with the gas-kinetic efficiencies or lower them by two orders of magnitude. The values k_S^{O2} (1.2·10^7 s^{-1}torr^{-1} (A) - 5·10^5 s^{-1}torr^{-1} (9,10-DCA) or 3.0·10^{11} mol^{-1}s^{-1}-1.2·10^{10} mol^{-1}s^{-1}) were larger than those in solutions for electron-donating substitutions with low E_{ox}, where values k_S^{O2} approached diffusion-controlled limit (2.6-3.1 10^{10} M^{-1}s^{-1}). However, a clear deviation from this behavior was observed in the case of cyano- and chlorosubstituted

ANTs with large value of E_{ox} [8], for which the k_S^{O2} decreased to $9-11 \cdot 10^9$ mol^{-1}s^{-1}, i.e. with decrease in the efficiency of CT interactions. In the gas-phase, the rate constants are expected to be larger for processes, limited by diffusion in solutions. Moreover, for gas phase systems, the absence of the effect of solvent reorganization energy also promotes to increase the rate constants of electron transfer.

The rate constants k_T^{O2} of PANs in vapor phase differed markedly from those in solution. (I) PANs showed the k_T^{O2} values varying within a wide range ($5 \cdot 10^2 - 4 \cdot 10^5$ s^{-1} Torr^{-1} or $1.2 \cdot 10^8 - 1.0 \cdot 10^9$ mol^{-1}s^{-1}) and smaller than those in neutral solutions ($k_T^{O2} = 3.1 \pm 0.4 \cdot 10^9$ mol^{-1} s^{-1} for A and its electron-donating substitutions and $5.2 \cdot 10^8$ mol^{-1} s^{-1} for 9,10-DCA)[4,5,8]). (II) The ratio k_S^{O2}/k_T^{O2} ($30 < k_S^{O2}/k_T^{O2} < 8 \cdot 10^2$) differed by several orders of magnitude for different PANs, while, in solutions, this ratio is frequently determined by the statistical spin factor (close to 9). (III) The value of k_T^{O2} was smaller by several orders of magnitude than the gas-kinetic rate constants ($4 \cdot 10^3 < k_{gk}^{O2}/k_T^{O2} < 3.5 \cdot 10^4$), however, in neutral solutions, the value $k_T^{O2} = 1/9\, k_{diff}$ corresponded to the upper limit to the quenching events. (IV) No pronounced dependence $k_T^{O2}(\Delta G_{et})$ was observed for a series of ANTs (A, 9-MA, 9,10-DBA) studied in cyclohexane, while, in the vapor-phase, the values of log k_T^{O2} decreased linearly with ΔG_{et} increase.

In the vapor-phase, the significant variations in the experimental k_S^{O2} and k_T^{O2} can be interpreted in terms of non-collision limited quenching ($k_{col} \geq k_S^{O2} \gg k_T^{O2}$). In solutions, the diffusion-controlled process obscures the variation of the actual quenching rate constants and their dependences on the molecular parameters. When in vapor phase the k_S^{O2} and k_T^{O2} decrease with increase in E_{ox}, it may be suggested that the deactivation stage of the collision complex leads to the formation of complexes, stabilized by CT with different stability and lifetime. Thus, E_{ox} is the most important parameter determining the quenching by O_2 and the complex stability of PANs with O_2.

The fraction of the singlet states q_S^{O2} and triplet states q_T^{O2} quenched in vapor phase by O_2 ($0.01 < q_S^{O2} < 0.75$; $0.12 < q_T^{O2} < 0.98$) were dependent on ΔG_{et} (TABLE 1). The q_S values, distinctly smaller than unity were often found in solutions and were explained by the competition between all oxygen quenching pathways and the intramolecular deactivation processes[2]. Despite the long lifetimes of triplets, the fraction q_T (0.98 (Phen, 2-AA)-0.12 (9,10-DCA)) approaching to be near unity only for PANs with low ΔG_{et}, while, in solutions, the q_T^{O2} values obtained for PANs under consideration varied within the range (0.9-0.6)[4,6]. Conclusion was made that in the vapor phase, the changes in q_S^{O2} and q_T^{O2} depend more strongly on complex stability, or, in other words, on the redox properties of colliding partners. In the gas phase as the most non-polar medium, there is no a solvent cage stabilizing the complexes. Therefore the conditions for the complex formation and dissociation differ from the corresponding conditions in solutions.

The temperature influence on the oxygen quenching rate constants have not been examined widely for gas-phase systems[2], although it is of great interest to elucidate the mechanism of the oxygen quenching reactions and to verify the theoretical models. The data obtained have shown that the temperature dependences for both the rate constants of the singlet and triplet states are similar. For different PANs the negative temperature dependences as well as the absence of temperature dependences for the oxygen quenching rate constants were observed over the same temperature range. For example, the activation energy estimated from the temperature-dependent rate constants proved to be negative for the fluorescence quenching of phenanthrene (E= -125 cm^{-1}), anthracene (Ea= -550 cm^{-1}), carbazole (Ea= -570 cm^{-1}). For triplet states quenching of phenanthrene, anthracene, chrysene and fluoranthene the activation energies are close to zero. These data are in contrast with the original Markus theory, which predicts the emergence of a positive activation barrier in all cases and a strong temperature dependence in the "inverted" region. Excited-state electron transfer reactions are commonly considered as ones controlled by activation energies that are necessary for a preliminary reorganization of medium and reactants. The conventional interpretation of activation barrier in electron transfer reactions was reconsidered in[18]. It was shown that actually the reaction rate is controlled by the enthalpy of the transient complex formation and activation energy of its decay by dissociation into final products of electron transfer, intersystem crossing and internal conversion. According to this theory[18], the temperature

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dependences for oxygen quenching rate constants of PAN excited states can be interpreted as a result of manifestation of the concerted mechanism for the electron transfer, which corresponds to the simultaneous electron translocation and reactant reorganization during the quenching process in the heated vapors.

4. CONCLUSIONS

I. In the PANs vapor, the oxygen-quenching rate constants k_S^{O2} ($1.2 \cdot 10^7$ s^{-1} torr^{-1} (A)-$4 \cdot 10^5$ s^{-1} torr^{-1} (9,10-DCA)) and k_T^{O2} ($5 \cdot 10^2$ s^{-1} Torr^{-1}-$4 \cdot 10^5$ s^{-1} Torr^{-1}) were found to vary within a wide range, namely from the values close to gas kinetic ones to the values that are smaller by four orders of magnitude. The k_S^{O2} values obtained were substantially larger but k_T^{O2} values were smaller than those for neutral solutions where quenching PANs excited states is frequently diffuson-controlled.

II. Based on the fact that log $k_{S(T)}^{O2}$ increases linearly with increasing exothermisity of the process of the full electron transfer, it was established the importance of the interactions with partial CT character for the oxygen quenching of PANs excited states in the vapor-phase.

III. In the heated vapors of PANs the oxygen quenching rate constants either change with temperature growth or show weak negative temperature dependences that are considered as a result of formation of CT complexes (PAN$^{\delta+}$O$_2^{\delta-}$) with the partial CT character and explained by the mechanism of the simultaneous electron translocation and reactant reorganization during the quenching process in the heated vapors.

ACKNOWLEDGMENTS

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