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Electron transfer in the photochemical reactions of phenothiazine with halomethanes

K. B. Petrushenko,★ L. V. Klyba, V. I. Smirnov, and S. G. Shevchenko

Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 39 6046. E-mail: admin@irioch.irk.ru

Photochemical transformations of phenothiazine (PTA) in solutions of halomethanes CH_nX_{4-n} (X = Cl, Br; n = 0, 1, 2) and in n-hexane—CH_nX_{4-n} mixtures under the irradiation with λ = 337 and 365 nm were studied. The rate constants of quenching of PTA fluorescence with halomethanes (k_q) are $4 \cdot 10^5$—$1.3 \cdot 10^{10}$ L mol^{-1} s^{-1}. The process occurs due to electron transfer with the C—X bond cleavage in the radical anion fragment of the primary radical ion pair. This results in the formation of the stable radical cation salt ($PTA^{\cdot +}X^-$). The plot of k_q *vs.* free energy of electron transfer corresponds to the Rehm—Weller empirical equation for a one-electron process and is satisfactorily described in terms of the theory of nonradiative electron transitions in the approximation of one quantum vibration.

Key words: phenothiazine, halomethanes, electron transfer, kinetics, fluorescence, nanosecond laser photolysis.

Great attention is given to the properties of radical anions of halomethanes ($RX^{\cdot -}$) and precisely to the fact of their existence as individual particles.[1—3] It is considered that, when an electron is transferred to the halomethane molecule, it "instantly" (within several oscillations) eliminates the X^- anion.[4] Distinction between the σ^*-$RX^{\cdot -}$ radical ion and $R^{\cdot} \cdot X^-$ complex formed in the solvent cage during the C—X bond cleavage is under discussion.[5] Quantum-chemical calculations of the $MeCl^{\cdot -}$ radical anion give contradictory results. According to calculations in Ref. 6, the radical anions exist as individual particles, and according to Ref. 7, the structure of the radical anions corresponds to the loose $Me^{\cdot} \cdot Cl^-$ complex. In the last case, a higher reorganization energy can be expected on going from the neutral molecule to the radical anion. These specific features stimulate an interest in studying photochemical reactions with RX including the electron transfer step. It has been established for a wide range of halohydrocarbons that the rate constants of halogen transfer to metal-centered radicals correlate with potentials of the electrochemical reduction of RX and are well described by the Rehm—Weller empirical equation for electron transfer.[8] However, the quenching rate constants of the triplet state of *N,N,N′,N′*-tetramethyl-*p*-phenyldiamine with halogen-containing acceptors do not correlate with the free energy of the process.[9]

In this work, we studied the reactions of phenothiazine (PTA) in the singlet and triplet electron-excited states, which in many cases manifest strong electron-donating properties,[10] with the acceptors CBr_4, $CHBr_3$, CH_2Br_2, CCl_4, $CHCl_3$, and CH_2Cl_2, whose electron affinities increase with an increase in the degree of halogenation and on going from chlorocarbons to bromo analogs.[1]

Experimental

Steady-state photolysis was carried out by a DRSh-500 mercury lamp. Excitation was performed at 365 nm (combination of the UFS-2 and SZS-21 light filters ($\Delta\lambda_{0.5}$ = 40 nm)), which corresponds to the edge of the long-wave absorption band of phenothiazine (λ_{max} = 320 nm). Only PTA was subjected to excitation. A cell with the 5-cm water layer was used as the thermal filter.

In laser photolysis the sample was excited using an AL-202 N_2 laser (λ = 337.1 nm, pulse energy 3 mJ, pulse duration at the half-height $\Delta t_{1/2}$ = 7 ns). The experimental technique was described in Ref. 10.

Spectrophotometric and fluorimetric measurements were carried out on Specord M-40 and Specord UV-VIS spectrophotometers and the luminescence experimental setup.[11] The sample was excited at a right angle through a DMP-4 monochhromator with light of a DRSh-500 mercury lamp. An MDR-3 monochromator was used as an analyzing instrument.

The rate of the source photoemission at λ = 365 nm was measured by an LM-2 thermoelectric receiver. The photoabsorption rate of PTA in the ground state per unit volume was calculated from the surface area of irradiation of the cell with the sample and the absorbance per cm at λ = 365 nm using the formula

$$I_a(t) = (2300 I_0(t)\varepsilon(\lambda_{ex})/S)[PTA]_0 \equiv \alpha[PTA]_0,$$

where $I_0(t)$ is the photoemission rate from the source, $\varepsilon(\lambda_{ex})$ is the molar absorptivity of phenothiazine at the excitation wavelength, and S is the surface area of irradiation of the cell. Dilute solutions with concentrations of ~10^{-4} mol L^{-1} were used.

Mass spectra were obtained on an LKB-2091 MS-CL spectrometer using direct injection at an ionization energy of 14 eV.

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Solvents CCl_4, $CHCl_3$, CH_2Cl_2, $CHBr_3$, CH_2Br_2, and *n*-hexane (99.9%, Merck) were purified by a standard procedure[12]; and CBr_4 (>98%, Merck) was used as received. Phenothiazine (>99%, Merck) was purified by multiple vacuum sublimation. Before experiment, freshly prepared solutions were purged with pure argon for 10 min in the dark.

Results and Discussion

Steady-state photolysis. Solutions of phenothiazine in halomethanes are photochemically unstable. Bands with λ_{max}/nm: 438, 486, 506, 524, and 726 (Figs. 1 and 2) corresponding to the absorption of the phenothiazine radical cation ($PTA^{\cdot+}$) appear in the spectra of PTA in $CHCl_3$ and CH_2Cl_2 at the early stage of photochemical reaction development. Similar spectra of $PTA^{\cdot+}$ were obtained by independent authors[13–15] using different methods for their generation. Further irradiation of solutions results in the fast, especially in the case of $CHCl_3$, disappearance of the $PTA^{\cdot+}$ absorption bands and appearance of new bands related to the formation of subsequent products. The mass spectra (EI, 14 eV) of a mixture of the final products contain peaks of molecular ions of mono-, di-, tri-, tetra-, and pentachlorophenothiazines with *m/z* 233, 267, 301, 335, and 369 (calculated per ^{35}Cl), which indicate the photochemical PTA halogenation. The consecutive formation of the halogenation products was observed. For example, dichloro-derivatives are formed by the excitation of monochlorophenothiazines, which is confirmed by the molecular peak with *m/z* 267 in its mass spectrum and new absorption bands in the UV spectrum at λ_{max} = 443 and 534 nm (see Fig. 1). A similar bathochromic shift in the spectra of $PTA^{\cdot+}$ was observed when the H atoms in the cycle were consecutively replaced by halogen atoms.[14] In the dark (when irradiation was ceased at the moment of achievement of the $PTA^{\cdot+}$ concentration sufficient for observation), the $PTA^{\cdot+}$ radical cations are very stable and can be detected within more than 48 h.

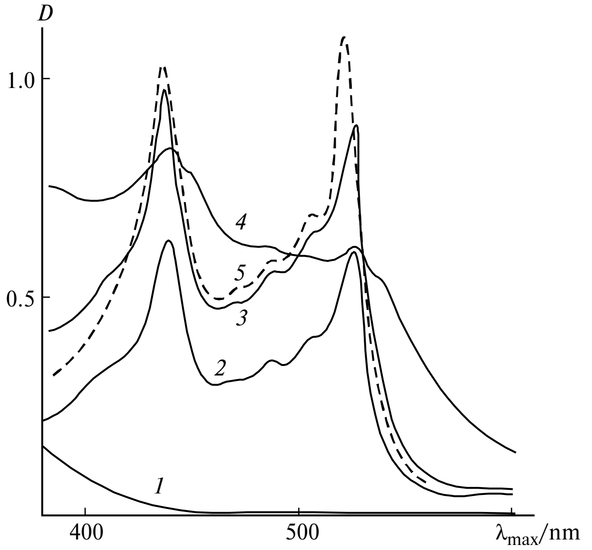


Fig. 1. Absorption spectra of phenothiazine ([PTA] = $3.5 \cdot 10^{-4}$ mol L^{-1}) in $CHCl_3$ under UV irradiation of the solution for different periods (s): *1*, 0; *2*, 10; *3*, 30; and *4*, 400. The absorption spectrum of the PTA + $SbCl_5$ system in CH_2Cl_2 without irradiation is presented for comparison (*5*).[13]

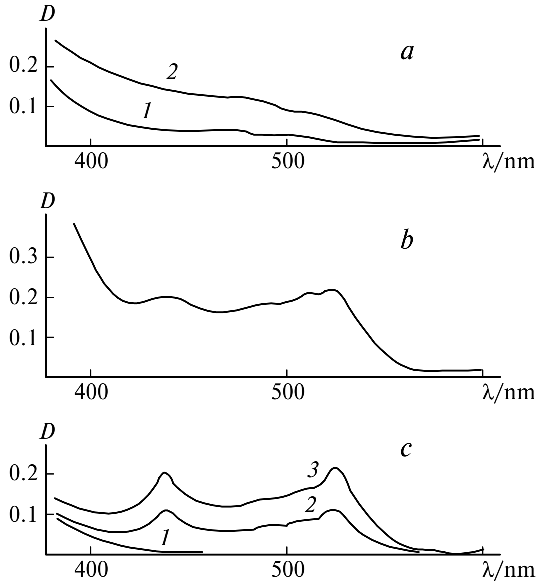


Fig. 2. Absorption spectra of phenothiazine ([PTA] = $2.8 \cdot 10^{-4}$ mol L^{-1}): *a*, continuous UV irradiation of the solution in CCl_4 for the time (s): *1*, 60; and *2*, 600; *b*, intermittent irradiation in CCl_4; *c*, continuous irradiation in CH_2Cl_2 for the time (s): *1*, 0; *2*, 120; and *3*, 240.

A solution of phenothiazine in CCl_4 is also unstable under irradiation. However, no absorption band of $PTA^{\cdot+}$ was observed in the spectra of the corresponding photolyzed mixtures under steady-state photolysis (see Fig. 2). We were able to detect spectrally the phenothiazine radical cation in this solvent only under intermittent irradiation of the solution with short, rather powerful pulses from an N_2 laser with an interval between them of ~1 s. After several flushes, the typical bands of $PTA^{\cdot+}$ with the main maxima at 438 and 525 nm appear in the electronic absorption spectra.

Similar results were obtained under irradiation of phenothiazine in CH_2Br_2 and $CHBr_3$, as well as for the PTA+CBr_4 system in *n*-hexane.

Thus, photoexcitation of phenothiazine in the presence of halomethanes produces the PTA radical cations and indicates the photochemical electron transfer from the phenothiazine molecule to the corresponding halomethane.

Electron transfer can occur due to the excitation of the charge transfer complex (CTC) or during dynamic quenching of the electron-excited state of phenothiazine. In the general case, the lifetimes of the primary singlet states lie in the nanosecond and subnanosecond time intervals. The lifetimes of similar triplet species can lie in the microsecond interval. It is reasonable to assume that relatively stable $PTA^{\cdot+}$ in nonpolar and poorly polar media of halomethanes are ion pairs (IP) ($PTA^{\cdot+}X^-$) similar to stable radical cation salts of phenothiazine, such as $PTA^{\cdot +}Br^-$, prepared by the synthetic method.[16]

Laser photolysis and fluorescence. To elucidate the nature of the reactive excited state of PTA, we studied the triplet-triplet absorption and fluorescence of PTA in an *n*-hexane solution with halomethane additives.

The PTA molecules in the triplet state (^{3}PTA, λ_{max} = 460 nm, $\varepsilon_{max} = 2.7 \cdot 10^4$ L mol^{-1} cm^{-1})[17] are inert toward halomethanes RX. None of the acceptors used in the work at concentrations ≤ 1 mol L^{-1} results in ^{3}PTA quenching (lifetime 100 ns). At the same time, the bands of $PTA^{\cdot +}$ with λ_{max} = 438 and 525 nm appear in the absorption spectra. The strong superposition of the bands of PTA T—T absorption on a relatively low-intensity absorption of $PTA^{\cdot +}$ impedes quantitative analysis, but it is clear that $PTA^{\cdot +}$ and ^{3}PTA are formed almost simultaneously within the laser pulse.

The fluorescence intensity of PTA in *n*-hexane decreases with an increase in the concentration of halomethanes in a solution, which indicates the participation of the singlet-excited state of phenothiazine (^{1}PTA) in the reaction.

Kinetic analysis. On the basis of the obtained results and published data,[9] the following kinetic scheme of the reaction can be proposed:

$$\mathrm{PTA} \xrightarrow{I_a(t)} {}^1\mathrm{PTA}, \quad (1)$$

$$^1\mathrm{PTA} \xrightarrow{k_0} \mathrm{PTA}, \quad (2)$$

$$^1\mathrm{PTA} + \mathrm{R{-}X} \xrightarrow{k_1} [(\mathrm{PTA}^{\cdot +}\mathrm{X}^-)\mathrm{R}^\cdot] \xrightarrow{k_p} \longrightarrow \text{Products.} \quad (3)$$

Equation (2) reflects the photophysical channel of quenching with $k_0 = k_d + rk_q[\mathrm{RX}]$, where $k_d = k_f + k_{isc} + k_{ic}$ is the rate constant of deactivation of the singlet-excited state in the absence of a quenching agent; k_f, k_{isc}, and k_{ic} are the rate constants of fluorescence, intersystem crossing, and internal conversion, respectively. Equation (3) describes the photochemical quenching channel, where $k_1 = sk_q$. The factors r and s reflect the contributions of these processes to the overall quenching rate constant k_q, so that $r + s = 1$; k_p is the rate constant of formation of the reaction products.

Under continuous irradiation, the kinetic scheme (see reaction equations (1)—(3)) suggests the following time dependence of the PTA, ^{1}PTA, and $(PTA^{\cdot +}X^-)$ concentrations:

$$[\mathrm{PTA}]_t = [\mathrm{PTA}]_0 \exp[-\alpha k_1[\mathrm{RX}]t/(k_0 + k_1[\mathrm{RX}])], \quad (4)$$

$$[^1\mathrm{PTA}]_t = \frac{\alpha[\mathrm{PTA}]_0}{k_0 + k_q[\mathrm{RX}]} \exp\left(-\frac{\alpha k_1[\mathrm{RX}]t}{k_0 + k_1[\mathrm{PTA}]_0}\right), \quad (5)$$

$$[(\mathrm{PTA}^{\cdot +}\mathrm{X}^-)]_t = \frac{[\mathrm{PTA}]_0}{1 - \dfrac{k_0 k_p}{\alpha k_1[\mathrm{RX}]} - \dfrac{k_p}{\alpha}} \times \left[\exp(-k_p t) - \exp\left(-\frac{\alpha k_1[\mathrm{RX}]t}{k_0 + k_1[\mathrm{RX}]}\right)\right]. \quad (6)$$

It is seen from Eq. (5) that the fluorescence rate ($k_f[^1\mathrm{PTA}]_t$) in the presence of a quenching agent depends on time and decreases due to PTA consumption during photolysis rather than to dynamic quenching.

Under these conditions, the relative quantum yield of fluorescence (Φ_0/Φ) depends on the photolysis duration.

In addition, photolysis results in the formation of the products with a sufficiently intense fluorescence, whose spectrum overlaps the emission spectrum of PTA. It is possible to correctly determine the quantum yield of phenothiazine fluorescence as a function of the RX concentration under PTA excitation with short pulses from a relatively low-power (LGI-21) N_2 laser, whose radiation parameters were chosen from the condition $\alpha\Delta t_{1/2} \ll 1$. The ratio of fluorescence quantum yields in the presence and absence of a quenching species is expressed by Eq. (7), which coincides with the standard Stern—Volmer equation for photophysical quenching

$$\Phi_0/\Phi \approx 1 + K[\mathrm{RX}], \quad (7)$$

where $K = k_1/k_0 = k_q/k_d$ is the Stern—Volmer constant.

The plots of Φ_0/Φ *vs.* concentration of halomethanes are linear (Fig. 3). The quenching rate constants calculated from the corresponding K values and previously[11] determined by us k_d for phenothiazine equal to $6.7 \cdot 10^8$ s^{-1} are presented in Table 1.

The influence of the $CHCl_3$ and CH_2Cl_2 concentrations on the rate of the absorbance increase (V_D) in the region of $PTA^{\cdot +}$ absorption in the initial portion of the

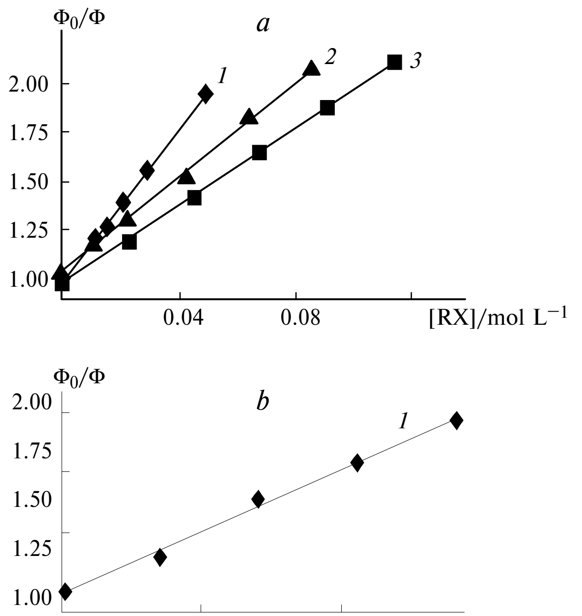


Fig. 3. Influence of the concentration of halomethanes on the relative quantum yield of fluorescence (Φ_0/Φ) of phenothiazine ([PTA] = $2.9 \cdot 10^{-4}$ mol L^{-1}) in *n*-hexane: *a*: *1*, CBr_4; *2*, CCl_4; and *3*, $CHBr_3$; *b*: *1*, $CHCl_3$.

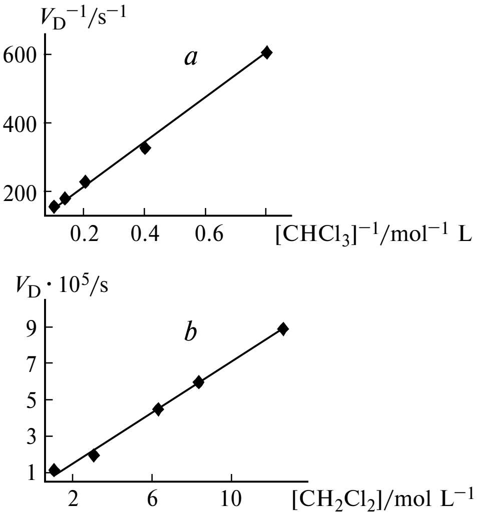


Fig. 4. Plots of the rate of absorbance increasing at λ = 520 nm during the photoconversion of phenothiazine ([PTA] = $7.4 \cdot 10^{-4}$ mol L^{-1}) *vs.* concentration of $CHCl_3$ (*a*) and CH_2Cl_2 (*b*) in *n*-hexane.

kinetic curve is shown in Fig. 4. In the case of dichloromethane, this plot is linear in the whole range of the concentrations

$$V_D = a[CH_2Cl_2], \tag{8}$$

whereas for quenching with trichlormethane the plot is nonlinear and can be linearized in the $1/V_D$—$1/[RX]$ coordinates

$$1/V_D = b + c/[CHCl_3], \tag{9}$$

where $a = 0.71$, $b = 79.64$, and $c = 657.42$; l is the thickness of the solution layer.

According to Eq. (6), the rate of the $PTA^{\cdot+}$ absorbance increase as a function of the concentration in the initial region of the kinetic curve can be presented as follows:

$$V_D(t_0 \approx 0) = s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0\frac{K[RX]}{1+K[RX]}, \tag{10}$$

and after transformation

$$\frac{1}{V_D} = \frac{1}{s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0} + \frac{1}{s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0K}\cdot\frac{1}{[RX]}, \tag{11}$$

where l is the layer thickness, and $\varepsilon^{\cdot+}(\lambda)$ is the molar absorption coefficient of $(PTA^{\cdot+}X^-)$.

A comparison of Eqs. (8) and (10) shows that $a = s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0K$ (under the condition that $K[RX] \ll 1$ for all [RX]). It follows from Eqs. (9) and (11) that $b = s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0$ and $c = s\alpha\varepsilon^{\cdot+}(\lambda)l[PTA]_0/K$. The a, b, and c coefficients obtained by us along with the known α, l, and $[PTA]_0$ values allow the determination of K and estimation of $s\varepsilon^{\cdot+}(\lambda)$. At λ = 520 nm, $s\varepsilon^{\cdot+} = 6700$ L mol^{-1} cm^{-1}, which is comparable with the molar absorptivity of the most intense absorption band of $PTA^{\cdot+}$ in the visible region (7940 L mol^{-1} cm^{-1} in MeCN).[18] Thus, the s factor is probably close to unity. The k_q coefficients obtained from K for $CHCl_3$ and CH_2Cl_2 are presented in Table 1. The closeness of the quenching constants for $CHCl_3$, obtained by two different methods, indicates that $(PTA^{\cdot+}X^-)$ is formed by fluorescence quenching.

Table 1. Kinetic parameters of the quenching process of PTA fluorescence at 298 K and acceptor properties of halomethanes

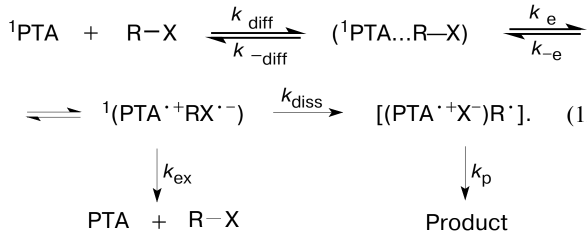
RX	K /L mol^{-1}	$k_q \cdot 10^{-9}$ /L mol^{-1} s^{-1}	$-E_{LUMO}$[a]	$-(E_d - EA)$[a]
			eV	
CBr_4	18.70	12.5	5.49	1.22
$CHBr_3$	9.70	6.5	5.37	0.92
CH_2Br_2	12.00	8.0	4.97	0.66
CCl_4	11.90	7.9	4.61	0.44
$CHCl_3$	0.25	0.17	4.39	0.27
	0.12[b]	0.08[b]		
CH_2Cl_2	0.0055[b]	0.00037[b]	3.81	0.10

[a] The E_{LUMO} and E_d values are taken from Ref. 1, the *EA* values are taken from Ref. 12.

[b] The data were obtained from the rate of an increase in the absorbance of $PTA^{\cdot+}$ at λ = 520 nm.

The rate constants of ^{1}PTA quenching with chloromethanes increase consecutively with an increase in the degree of methane chlorination tending to the diffusion limit, which is $2 \cdot 10^{10}$ L mol^{-1} s^{-1} for *n*-hexane. For bromo analogs, the k_q values depend weakly on the degree of bromination (see Table 1).

The energy of LUMO of the studied halocarbons decreases successively when both Cl is replaced by Br and the degree of halogenation increases (see Table 1). The electron affinity of these halomethanes should increase in the same order.[1] The experimentally observed change in the k_q value, depending on the electron affinity of the quenching agent, is characteristic of quenching reactions *via* electron transfer



$$\begin{tikzcd} {}^1\mathrm{PTA} + \mathrm{R{-}X} \arrow[r, shift left, "k_{\mathrm{diff}}"] & ({}^1\mathrm{PTA...R{-}X}) \arrow[l, shift left, "k_{-\mathrm{diff}}"] \arrow[r, shift left, "k_e"] & {}^1(\mathrm{PTA}^{\cdot+}\mathrm{RX}^{\cdot-}) \arrow[l, shift left, "k_{-e}"] \arrow[r, "k_{\mathrm{diss}}"] \arrow[d, "k_{\mathrm{ex}}"] & {[(\mathrm{PTA}^{\cdot+}\mathrm{X}^-)\mathrm{R}^\cdot]} \arrow[d, "k_p"] \\ & & \mathrm{PTA} + \mathrm{R{-}X} & \mathrm{Product} \end{tikzcd} \tag{12}$$

Here (^{1}PTA...R—X) is the collision complex, and $^1(PTA^{\cdot+}RX^{\cdot-})$ is the primary RIP. Under the quasi-steady-state approximation with respect to the collision complex and RIP concentrations, the following correlations between the rate constants are valid:

$$\begin{gathered} k_0 = k_d + k_{ex}k_q[RX]/(k_{ex} + k_{diss}), \\ k_1 = k_{diss}k_q/(k_{ex} + k_{diss}), \\ k_q = \frac{k_{diff}}{1+(k_{-diff}/k_e)[1+k_{-e}/(k_{ex}+k_{diff})]}, \\ r = k_{ex}/(k_{ex} + k_{diss}),\ s = k_{diss}/(k_{ex} + k_{diss}). \end{gathered} \tag{13}$$

The lifetime of RIP is determined by the lifetime of the radical anion component $RX^{\cdot -}$, which is indicated by the obtained value of the factor $s \approx 1$. Since $s = k_{diss}/(k_{ex} + k_{diss})$, then $k_{diss} > k_{ex}$ and the lifetime of RIP is $\sim 1/k_{diss}$. Experiments with picosecond time resolution give the upper limit of $CCl_4^{\cdot -}$ decay equal to 18 ps.[19] Thus, it is most likely that the lifetime of $^1(PTA^{\cdot +}\ RX^{\cdot -}) \le 18$ ps.

Energy parameters of the reaction. The change in the free energy during the electron transfer reaction in the collision complex with the formation of a relaxed RIP (ΔG_e) can be estimated from the correlation[20]

$$\Delta G_e = IP - EA - E^* - (\mu^2/\rho^3)(\varepsilon - 1)/(2\varepsilon + 1) - e^2/d - T\Delta S, \qquad (14)$$

where IP is the ionization potential of the donor, EA is the electron affinity of the acceptor, E^* is the electron excitation energy of the donor (or acceptor), μ is the dipole moment, ρ is the radius, d is the distance between ions in the primary RIP, ε is the dielectric constant, and ΔS is the change in entropy. This correlation also takes into account the solvation energy of RIP in a medium with the dielectric constant ε and the energy of the Coulomb interaction between ions in RIP.

Presently, the question about the structure of the primary relaxed RIP (whether the radical anion is an individual particle or the weakly linked loose $R^{\cdot} \cdot X^-$ complex with the C—X distance > 3 Å)[21] has no answer. Nevertheless, we believe that the change in the standard free energy for RIP formation in the case of one-electron donor and several related RX can be written in the following form:

$$\Delta G_e = C - EA(RX), \qquad (15)$$

where C is the general parameter, and $EA(RX)$ is the electron affinity of halomethane.

Experimental values of the electron affinity of halomethanes are virtually lacking in literature, and those for CCl_4 (0.15 and 0.93,[22] 2.12 [23]) and CBr_4 (1.17 and 1.95,[22] 2.06 [23]) differ substantially. Therefore, the electron affinity of the RX used was determined from the cycle

$$\begin{tikzcd}
RX \arrow[r, "E_d(RX)"] \arrow[d, "EA(RX)"'] & RX^{\cdot} + X^{\cdot} \arrow[d, "EA(X)"] \\
RX^{\cdot -} \arrow[r, "E_d(RX^{\cdot -})"'] & RX^{\cdot} + X^{-}
\end{tikzcd}$$

using the formula

$$EA(RX) = EA(X) - E_d(RX) + E_d(RX^{\cdot -}) \approx EA(X) - E_d(RX),$$

where $E_d(RX)$ and $E_d(RX^{\cdot -})$ are the energies of C—X bond dissociation in the corresponding halomethane and its radical anion, and $EA(X)$ is the electron affinity of the halogen atom. Since the radical anion states of halomethanes are very unstable, the $E_d(RX^{\cdot -})$ values were accepted to be zero in calculation of the electron affinity. The validity of this approximation is confirmed by the linear dependence of the $EA(X) - E_d(RX)$ difference on such a parameter of electron affinity as E_{LUMO} (Fig. 5) and the closeness of the absolute EA values for CCl_4 (0.44 eV) and CBr_4 (1.22 eV) to the values obtained from the frequency of the CTC absorption bands (0.15 and 1.17 eV, respectively).[22]

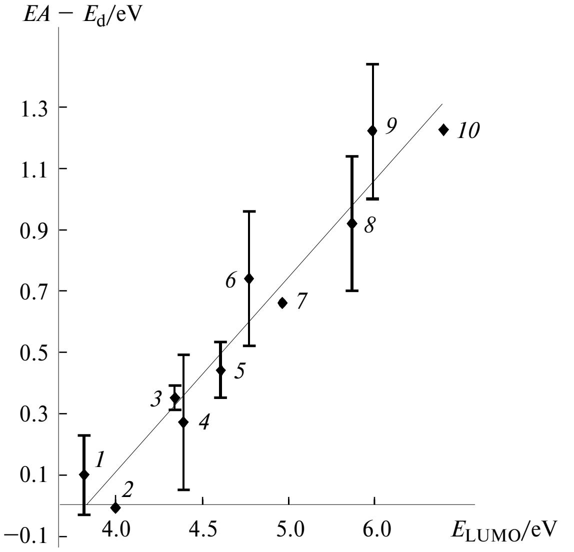


Fig. 5. Correlation between the $EA - E_d$ difference and E_{LUMO} for CH_2Cl_2 (*1*), CH_3Cl (*2*), CH_3Br (*3*), $CHCl_3$ (*4*), CCl_4 (*5*), CH_3I (*6*), CH_2Br_2 (*7*), $CHBr_3$ (*8*), CBr_4 (*9*), and CI_4 (*10*). The E_d and E_{LUMO} values were taken from Ref. 1, the EA values are available in Ref. 12.

The plot of the logarithms of quenching rate constants *vs.* $EA(X) - E_d(RX)$ difference is typical of photoinduced electron transfer (Rehm—Weller plot, Fig. 6). A sharp transition between the kinetic (a straight line with the slope angle $\cong 1/(2.3RT)$) and diffusion regimes of the reaction suggests a low value of the internal barrier (activation energy at $\Delta G_e = 0$) for electron transfer.

Quantitative description of electron transfer in terms of the correlation between the activation energy and

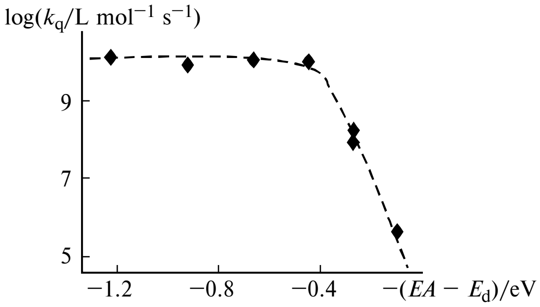


Fig. 6. Experimental (points) and calculated using Eq. (17) (dotted line) quenching rate constants (k_q) of PTA fluorescence by halomethanes in n-hexane at different $EA - E_d$ values and optimum values of the parameters.

free energy of the reaction was performed by us using the empiric Rehm—Weller equation[24]

$$\Delta G_e^{\neq} = \Delta G_e/2 + [(\Delta G_e/2)^2 + \Delta G^{\neq}{}_{RW}(0)^2]^{0.5}, \qquad (16)$$

where $\Delta G^{\neq}{}_{RW}(0)$ is the internal barrier, and expressions for the quenching rate constant (13) are used under the assumption that $k_{-e}/(k_{ex} + k_{diss}) << 1$ and $k_e = k_{e0}\exp(-\Delta G_e^{\neq}/k_B T)$. Then it follows from Eqs. (16) and (13) that

$$k_q = k_{diff}/\{1 + A\exp[-(\Delta G_e/2 + [(\Delta G_e/2)^2 + \\ + \Delta G_{RW}{}^{\neq}(0)^2]^{0.5})/k_b T]\}, \qquad (17)$$

where $A = k_{-diff}/k_{e0}$ and $\Delta G_e = C - [EA(X) - E_d(RX)]$.

Approximation of the experimental data by correlation (17) using the nonlinear regression method[25] with variation of three parameters A, C, and $\Delta G^{\neq}{}_{RW}(0)$ (Fig. 6) gives $A = 0.5\pm0.3$, $C = (0.39\pm0.01)$ eV, and $\Delta G^{\neq}{}_{RW}(0) = (0.05\pm0.03)$ eV.

A good agreement between the experimental and calculated quenching rate constants indicates the validity of the assumption that the C parameter is constant in the RX series and, hence, the RIPs of all halomethanes have similar structures.

The $\Delta G_{RW}{}^{\neq}(0)$ parameter is empirical. According to the classical Marcus theory of electron transfer,[26] the following expression is valid:

$$\Delta G_e^{\neq} = E_r(1 + \Delta G_e/E_r)^2/4, \qquad (18)$$

where E_r is the reorganization energy. The classical approach can describe the recombination and charge separation processes in rigidly linked molecular structures but only for strongly endothermic reactions. For liquid-phase electron-transfer reactions in the inverted region, quantum effects should be taken into account. It is often assumed[27] that $\Delta G^{\neq}{}_{RW}(0) = (E_{rs} + E_{rv})/4$, where E_{rs} and E_{rv} are the reorganization energies of the external and internal spheres, respectively. Since for n-hexane in the dielectric continuum approximation $E_{rs} \approx 0$, then E_{rv} amounts to 0.2 eV, which is very low. A much higher reorganization energy is expected for the PTA + RX system because the electron transfer should be accompanied, from the one hand, by a considerable rearrangement of the PTA geometric configuration, which becomes more planar upon ionization, and on the other hand, by the dissociation of the covalent C—X bond in the anionic state of halomethane.

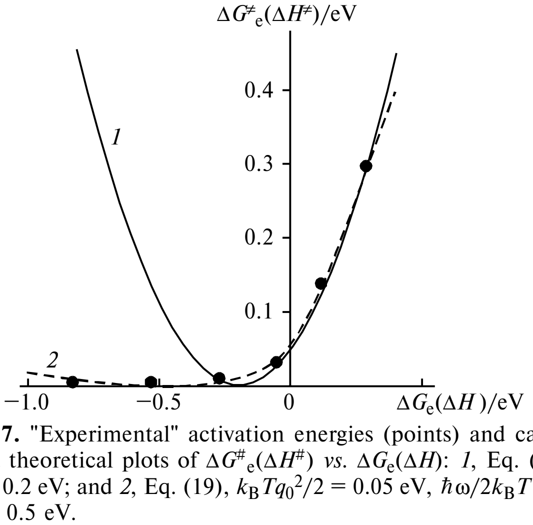


Fig. 7. "Experimental" activation energies (points) and calculated theoretical plots of $\Delta G^{\#}{}_e(\Delta H^{\#})$ *vs.* $\Delta G_e(\Delta H)$: *1*, Eq. (18), $E_r = 0.2$ eV; and *2*, Eq. (19), $k_B T q_0{}^2/2 = 0.05$ eV, $\hbar\omega/2k_B T = 5$, $E_r = 0.5$ eV.

The plot of $\Delta G_e^{\neq}$ *vs.* ΔG_e shows clearly that correlation (18) (Fig. 7, curve *1*) poorly reproduces the experimental results in the exothermic region of the reaction. A much better correspondence (see Fig. 7, curve *2*) is achieved when the semiclassical approximation is used

$$\begin{aligned}\Delta H^{\neq} = {} & \Delta H/2\{1 + (2k_B T/\hbar\omega)\ln[\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r + \\ & + \sqrt{(\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r)^2 + 1}]\} + \\ & + (k_B T q_0{}^2/2)[\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r + \\ & + \sqrt{(\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r)^2 + 1}] \times \\ & \times \mathrm{sh}(\hbar\omega/2k_B T)/[1 - (\Delta H/E_r)^2]/\{[\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r + \\ & + \sqrt{(\Delta H\,\mathrm{sh}(\hbar\omega/2k_B T)/E_r)^2 + 1}] \times \\ & \times [\mathrm{ch}(\hbar\omega/2k_B T) + (\Delta H/E_r)\mathrm{sh}(\hbar\omega/2k_B T)] + 1\}, \qquad (19)\end{aligned}$$

where $\Delta H^{\neq}$ is the activation energy, ΔH is the thermal effect of the reaction, $\hbar\omega$ is the frequency of the active mode, $E_r = \hbar\omega q_0{}^2/2$ is the reorganization energy, and q_0 is the shift of the active mode. Expression (19) is a particular case of the quantum-mechanical description of the probability of transition from the initial (i) to final (f) state,[28] taking into account only one active quantum vibration with a slightly changed frequency ($\omega_i = \omega_f$).

In the case of $\hbar\omega << k_B T$ (classical vibrations), Eqs. (19) and (18) coincide at $\Delta H^{\neq}(0) = E_r/4$. In the case of $\hbar\omega >> k_B T$ (quantum vibrations), the plot of $\Delta H^{\neq}$ *vs.* ΔH differs strongly from a parabola and approaches function (16) in a rather broad region of ΔH changing. Unlike the classical case, here $\Delta H^{\neq}(0) = k_B T q_0{}^2/2$ and it is proportional to the tunneling factor. The activation energy $\Delta H^{\neq}(0)$ is directly related to the reorganization energy of the system only under the approximation of one active vibration: $\Delta H^{\neq}(0) = k_B T E_r/\hbar\omega$ (involving several vibrational degrees of freedom $E_r = 0.5\Sigma\hbar\omega_i q_{0i}{}^2$, $\Delta H^{\neq}(0) = 0.5 k_B T \Sigma q_{0i}{}^2$). If we assume that $\Delta G^{\neq}{}_{RW}(0) = k_B T q_0{}^2/2$, then $E_r = \hbar\omega\Delta G^{\neq}{}_{RW}(0)/k_B T$ (and not $E_r = 4\Delta G^{\neq}{}_{RW}(0)$) and, since $\hbar\omega/k_B T >> 1$, the E_r value for the system under study is much higher than 0.2 eV. For example, the dotted line describing the experiment (see Fig. 7, curve *2*) was obtained at $E_r = 0.5$ eV.

This E_r value is rather low even comparable to E_r for molecular systems that do not require a considerable nuclear reorganization for electron transfer. For example, the $\Delta G^{\neq}{}_{RW}(0)$ value for electron transfer obtained from analysis of the rate constants of fluorescence quenching of 55 "classical" donor-acceptor systems is 2.4 kcal mol^{-1} ($\approx$0.1 eV).**[24]** Correspondingly, E_r is 0.4 eV when estimated by formula (18) and ~1 eV using formula (19). The low E_r value for the PTA—RX system can be attributed to the opposite influence of two factors: the strong splitting of the mode (increasing E_r) and a strong decrease in the frequency of the C—X bond vibration due to the transition RX $\rightarrow$ $R^{\cdot} \cdot X^-$ (decreasing E_r). The contribution of the phenothiazine moiety to the intrasphere reorganization of the system can also be smaller compared to that expected according to the differences in the geometry of the ground state of PTA and its radical cation. In fact, the absence of the vibrational structure of the long-wave PTA absorption band in the UV spectrum and the appearance of the pronounced vibrational structure in the fluorescence spectrum indicate a more planar configuration of PTA in the fluorescent state and, hence, a smaller reorganization of the system required for the ^{1}PTA $\rightarrow$ PTA$^{\cdot +}$ transition.

Thus, the quenching of phenothiazine fluorescence with halomethanes in *n*-hexane occurs *via* the electron transfer mechanism followed by the C—X bond cleavage in the radical anion of the corresponding halomethane and the formation of the stable PTA$^{\cdot +}$X$^-$ pair, which is close, most likely, to the radical cation salt of PTA. The plots of the rate constants of fluorescence quenching *vs.* free energy of the process do not differ in shape from the plots typical of one-electron transfer reactions.

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