Photophysical and Photochemical Studies of Polycyclic Aromatic Hydrocarbons in Solutions Containing Tetrachloromethane
II. The Solvent Effect on the Fluorescence Quenching of Aromatic Hydrocarbons by Tetrachloromethane

Wiesław M. Wiczk

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

Tadeusz Latowski

Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland

Z. Naturforsch. **42a**, 1290–1295 (1987); received June 22, 1987

Fluorescence quenching of aromatic hydrocarbons in a large concentration range of the quencher has been studied in a variety of two-component mixtures of tetrachloromethane with other solvents. In aliphatic solvents the process could be described by the Stern-Volmer equation, whereas in the remaining mixtures the fluorescence quenching curves showed a parabolic behaviour which has been explained in terms of specific interactions between the components of the mixtures.

1. Introduction

It has long been known that halomethanes, especially CCl_4, quench the fluorescence of aromatic hydrocarbons in solution [1 – 7]. This is accompanied by the appearance of free radicals whose generation provides the main pathway of the quenching [4, 8 – 10].

Lewis and Ware [11] have presented an extended model for the fluorescence quenching of aromatic hydrocarbons by CCl_4 including the influence of the wavelength of the exciting radiation on the quenching efficiency and the role of an exciplex, generating photoproducts.

In the preceding paper I [12] we measured the fluorescence quenching of anthracene in binary mixtures of CCl_4 with benzene, p-xylene or mesitylene. In these mixtures the relative quantum yield ϕ_0/ϕ as function of the CCl_4 concentration shows a parabolic curve. We interpreted this parabolic behaviour assuming two quenching species – free CCl_4 molecules and CCl_4-solvent molecular complexes – as quenchers having different quenching constants.

In this paper we present measurements on other fluorescing aromatics in three mixtures and on anthracene in mixtures of CCl_4 with seventeen different solvents. We discuss a second kinetic scheme – different from that discussed in paper I – which gives a parabolic concentration dependence, too.

2. Experimental

Anthracene and all the solvents were either of spectrograde purity or pure for fluorescence reagents and were used as supplied. The other hydrocarbons were purified by column chromatography on silica gel using a cyclohexane-benzene (1:1 and 2:1 *v/v*) mixture as the developing system. Their purity was monitored by TLC, the spots being detected under a mercury lamp equipped with an appropriate filter. Both the absorption and fluorescence spectra of the purified compounds resembled those reported in the literature.

The luminescence spectra were measured on a modular spectrofluorimeter according to Jasny [13], the absorption spectra with a Carl Zeiss Specord UV-VIS spectrophotometer.

The quantum yields ϕ we measured with quinine sulphate as a standard ($\phi = 0.51$ [14]), corrected for variations in the refractive index and absorbance readings due to varying composition of the solutions and for reabsorption. Some of the results are presented by the intensity ratio J_0/J. For excitation the mercury line 366 nm was used.

The fluorescence decay curves were measured by a sampling technique using an ns N_2-laser (at the

---

Reprint requests to Dr. T. Latowski, Institute of Chemistry, Pedagogical University, P-25-020 Kielce, Poland.

0932-0784 / 87 / 1100-1290 $ 01.30/0. – Please order a reprint rather than making your own copy.

Institute of Physical Chemistry, Polish Academy of Sciences). The lifetimes were determined by the plane-phase method [15].

3. Results

A) *The fluorescence quenching of the different hydrocarbons in two-component mixtures of CCl_4 with cyclohexane, benzene and acetonitrile.*

The fluorescence spectra of some aromatic hydrocarbons in the above two-component mixtures display no significant difference compared with those taken in the pure solvents. In CCl_4-cyclohexane and CCl_4-acetonitrile, the spectrum shifts slightly to the red only, increasing the CCl_4 concentration. No additional emission indicating the presence of other species, e.g. a hydrocarbon-CCl_4 exciplex, can be noted in the spectrum. In the CCl_4-cyclohexane mixture, the reciprocal relative fluorescence intensity J_0/J or quantum yield ϕ_0/ϕ grows monotonically with increasing CCl_4 concentration. In the CCl_4-benzene and CCl_4-acetonitrile mixtures, on the other hand, one observes a parabolic dependence with a maxmimum. This behaviour was observed for perylene, pyrene, anthracene, the 9,10-dimethyl-, 9,10-diphenyl-, 2-methyl-, and 9-methyl anthracene derivatives, for benz[a]anthracene and dibenz[a, h]anthracene. Examples are shown in Figures 1 – 5.

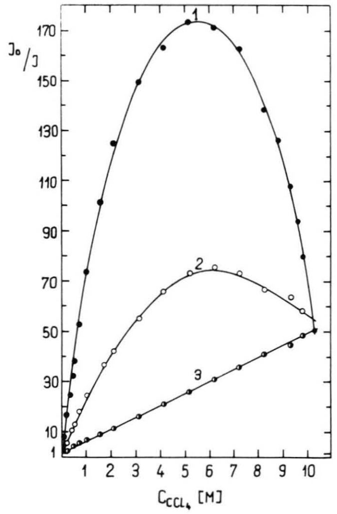


Fig. 1. Fluorescence quenching curves of 9,10-dimethylanthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in acetonitrile **1**, benzene **2**, and cyclohexane **3**.

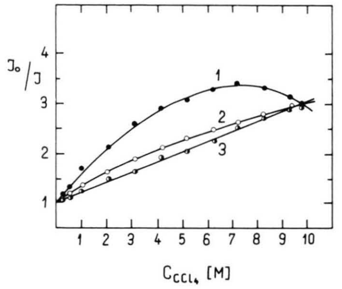


Fig. 2. Fluorescence quenching curves of dibenz[a, h]anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in acetonitrile **1**, benzene **2**, and cyclohexane **3**.

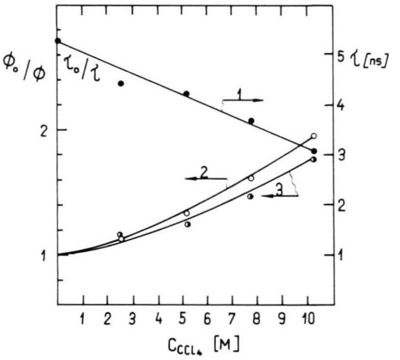


Fig. 3. Fluorescence lifetime of perylene **1** ($c = 3 \times 10^{-5}$ M) and the magnitudes of ϕ_0/ϕ (– ○ – ○ – ○ –) **2** and τ_0/τ (– ● – ● – ● –) **3** as functions of CCl_4 concentrations in the mixtures with cyclohexane.

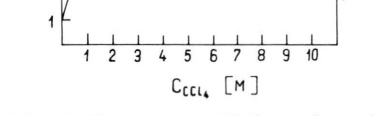


Fig. 4. Fluorescence lifetime of perylene **1** ($c = 3 \times 10^{-5}$ M) and the magnitudes of ϕ_0/ϕ (– ○ – ○ – ○ –) **2** and τ_0/τ (– ● – ● – ● –) **3** as functions of CCl_4 concentrations in the mixtures with benzene.

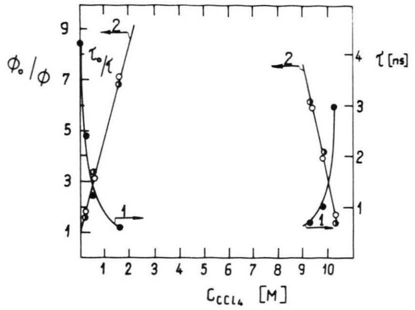


Fig. 5. Fluorescence lifetime of perylene **1** ($c = 3 \times 10^{-5}$ M) and the magnitudes of ϕ_0/ϕ (– ○ – ○ – ○ –) and τ_0/τ (– ● – ● – ● –) **2** as functions of CCl_4 concentrations in the mixtures with acetonitrile.

Most of them show the parabolic shape of the fluorescence quenching curves already reported for perylene [3] and anthracene [12]. Exceptions provide 9,10-diphenylanthracene and dibenz[a, h]-anthracene (Fig. 2) for which the relation $J_0/J = f[CCl_4]$ exhibits no peak, but merely a distinct curvature in the CCl_4-benzene mixture.

The linear Stern-Volmer equation can describe the fluorescence quenching by CCl_4 over the whole concentration range for the solvents cyclohexane and some related compounds only. In some cases a small positive deviation from the straight Stern-Volmer line is observed, indicating a contribution of a static quenching (Figure 6).

In the cases of a parabolic curve we calculated a Stern-Volmer quenching constant (K_{SV} Table 2) from the inclination at zero concentration.

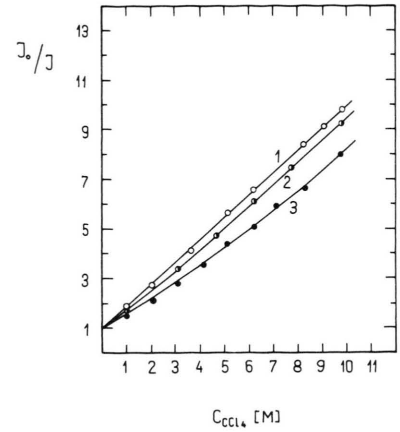


Fig. 6. Fluorescence quenching curves of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in methylcyclohexane **1**, n-pentane **2** and n-hexane **3**.

The efficiency of fluorescence quenching by the action of CCl_4 is strongly dependent on the polarity of the solvent, being the highest in acetonitrile and the lowest in cyclohexane, as well as on the nature of the fluorescing hydrocarbon, as shown by the results listed in Table 1.

B) *The solvent effect on the fluorescence quenching of anthracene by tetrachloromethane*

The fluorescence quenching of anthracene has been studied in seventeen mixtures of CCl_4 with the solvents named in Table 2 (the concentration of

Table 1. Parameters of the fluorescence quenching of aromatic hydrocarbons by CCl_4 in two-component mixtures with cyclohexane, benzene and acetonitrile $K_{SV} = k_q \tau_0 (M^{-1})$ for $[Q] \rightarrow 0$; k_q ($M^{-1} s^{-1}$).

Donor	Ionization potential IP (eV)	Cyclohexane $\varepsilon = 2.02$		Benzene $\varepsilon = 2.27$		Acetonitrile $\varepsilon = 37.5$	
		K_{SV}	$k_q \times 10^{-8}$	K_{SV}	$k_q \times 10^{-8}$	K_{SV}	$k_q \times 10^{-8}$
Anthracene	7.43	0.90	2.22	6.4	18.77	27.0	59.47
2-Methylanthracene	–	1.82	–	6.87	–	23.67	–
9-Methylanthracene	–	1.32	–	12.96	–	42.14	–
9,10-Dimethylanthracene	–	4.78	–	24.38	32.2[b,c]	72.22	–
9,10-Diphenylanthracene	7.53	1.20	–	3.40	7.36[b,c]	18.25	–
Pyrene	7.55	0.3	0.15[a]	5.6	–	15.2	6.13[b,d]
Perylene	7.07	0.037	0.070	0.60	1.19	3.93	9.33
Benz[a]anthracene	7.45	0.133	0.106[a]	1.08	–	3.67	–
Dibenz[a, h]anthracene	7.80	0.205	0.171[a]	0.38	–	0.68	–

[a] For calculations the fluorescence lifetimes in non-deaerated cyclohexane solutions were used as reported in [16].

[b] The fluorescence lifetimes in non-deaerated solutions were calculated from equation $1/\tau = 1/\tau_0 + k_q [O_2]$.

[c] τ_0 and k_q values as reported in [17] were used for calculations. The oxygen concentrations in benzene were taken from [18].

[d] τ_0 values were taken from [19], and those of k_q from [20]. Both the oxygen concentration in acetonitrile under the air pressure of 1 atm, and the oxygen content in the air (20.95%) were calculated from equation $[O_2] = 8 \times 10^{-3}$ p (atm) [21].

Table 2. Parameters of the fluorescence quenching of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in various solvents (non-deaerated solutions) $K_{SV} = k_q \tau$ (M^{-1}), k_q ($M^{-1} s^{-1}$), τ (ns)

Solvent	K_{SV}	$k_q \times 10^{-9}$		τ	ε[h]
		Found	Lit.		
n-Pentane	0.770	–	–	–	1.844
n-Hexane	0.580	0.136	0.21[f]	3.56[a,e]	1.894
Methylcyclohexane	0.903	–	–	–	2.020
Cyclohexane	0.908	0.224	0.19[f] 0.25[g]	4.06	2.023
Benzene	5.620	1.65	1.40[f]	3.41	2.284
p-Xylene	4.070	1.20	–	3.39[a,d]	2.270
Mesitylene	3.270	–	–	–	2.279
1,4-Dioxane	6.85	2.06	–	3.33[a]	2.235
Di-n-propyl ether	2.15	–	–	–	3.390
Ethyl acetate	8.55	–	–	–	6.060
Tetrahydrofuran	9.40	–	–	–	7.58
n-Butanol	6.26	1.34	–	4.67[a,c]	17.80
n-Propanol	8.53	1.82	–	4.70[a,c]	21.10
Acetone	15.11	4.06	–	3.72[a]	20.74
96% Ethanol	13.95	2.98	2.96[g]	4.68[a,b]	24.74
Methanol	16.27	3.72	3.70[f]	4.38[a]	32.6
Acetonitrile	25.80	5.68	6.03[f]	4.54	37.5

[a] Fluorescence lifetimes were calculated from $1/\tau = 1/\tau_0 + k_q [O_2]$; the τ_0 and k_q values were taken from [22] and the oxygen concentration from [18].
[b] The τ_0 and k_q values for 96% ethanol were assumed to be equal to those for the absolute ethanol.
[c] The τ_0 and k_q values were assumed the same as for the iso-compound.
[d] The concentration of oxygen in p-xylene was assumed to be equal to that in benzene.
[e] The τ_0 and k_q values were assumed to be equal to those for n-heptane.
[f] taken from [4].
[g] taken from [11].
[h] The ε (electric permeability or dielectric constant) values taken from [23].

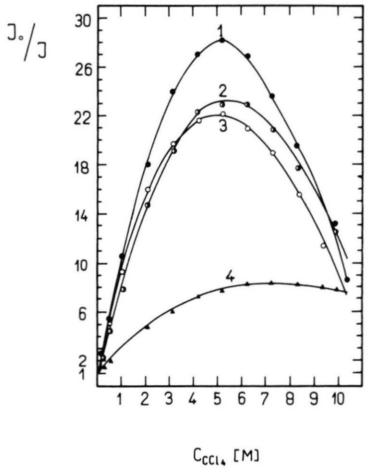


Fig. 7. Fluorescence quenching curves of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in tetrahydrofuran **1**, 1,4-dioxane **2**, ethyl acetate **3** and di-n-propyl ether **4**.

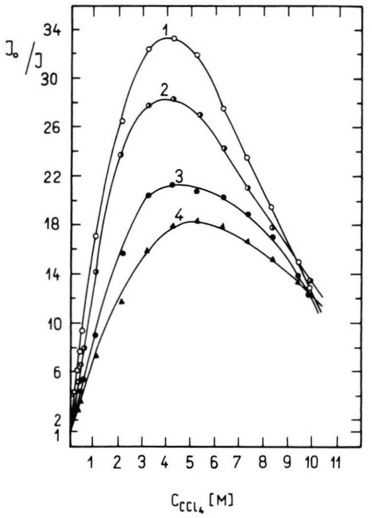


Fig. 8. Fluorescence quenching curves of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in methanol **1**, 96% ethanol **2**, n-propanol **3** and n-butanol **4**.

CCl_4 $0 \leqslant c \leqslant 10.24$ M). Some fluorescence quenching curves in these mixtures are shown in Figures 6–8.

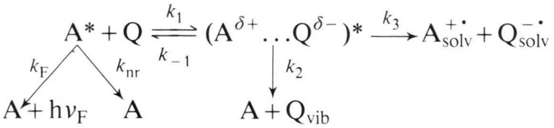
For solutions with aliphatic hydrocarbons only the fluorescence quenching curves can be described by the Stern-Volmer relation including the static quenching. For the remaining mixtures one gets a parabolic behaviour.

The interesting parameters of the fluorescence quenching of anthracene by CCl_4 in the various solvents are listed in Table 2.

4. Discussion

Going beyond older concepts, that the quenching rate constant of a hydrocarbon depends not only on its ionisation potential but also on its nature, the observed deviations from the Stern-Volmer equation in the mixtures of CCl_4 with benzene and acetonitrile on the one hand and the applicability of this equation in CCl_4-cyclohexane mixtures on the other suggest that the parabolic shape of the fluorescence quenching curves is an effect of intermolecular interaction between the components of the mixtures [12, 4].

The data of Table 2 show that the polarity of the solvent has a decisive effect on the mechanism of the fluorescence quenching. The quenching process and its non linearity are most pronounced in acetonitrile, having the highest electric permeability, and least in aliphatic hydrocarbons. The interpretation given in paper I [12] does not suffice to explain the strong dependence on the electric permeability. We suggest a share of a second process, described by the kinetic scheme



having a parabolic dependence on concentration, too.

In the above scheme k_F and k_{nr} describe the radiative and non radiative deactivation of the excited molecule, respectively. k_1 and k_{-1} are the rate constants for the formation and dissociation of an exciplex, k_2 and k_3 the rate constants for the loss of the exciplex excitation energy by energy transfer to the quencher molecule or by generation of a radical ion pair.

Solving the two kinetic equations

$$\frac{d}{dt}[A^*] = -(k_F + k_{nr} + k_1[Q])[A^*] + k_{-1}[(A\ldots Q)^*] + J = 0,$$

$$\frac{d}{dt}[(A\ldots Q)^*] = -(k_2 + k_3 + k_{-1})[(A\ldots Q)^*] + k_1[A^*][Q] = 0$$

for $[A^*]$ having a constant absorption rate J, one gets for the quantum efficiency ϕ:

$$\phi = \frac{k_F[A^*]}{J} = \frac{k_F}{k_F + k_{nr} + k_1 \dfrac{k_2 + k_3}{k_{-1} + k_2 + k_3}[Q]},$$

or for the relative reciprocal quantum efficiency:

$$\phi_0/\phi = 1 + \frac{k_1}{k_F + k_{nr}} \, \frac{k_2 + k_3}{k_{-1} + k_2 + k_3}[Q] .$$

As long as all rate constants are supposed to be independent of the concentration [Q] of the quencher molecules, ϕ_0/ϕ follows the Stern-Volmer relation.

But in mixtures with polar solvents, such as acetonitrile or methanol, CCl_4 acts not as quencher only but also as a component lowering the solvent polarity. We suppose the rate constants k_{-1} and k_3 for the dissociation of the complex to be sensitive to the variation of the solvent polarity, whereas we take k_1 and k_2 to be independent of [Q].

Setting as a first approximation

$$k_{-1}(Q) = k_{-10} + b[Q],$$
$$k_3(Q) = k_{30} - a[Q],$$

the relative reciprocal quantum efficience can be written in the nearly parabolic form

$$\phi_0/\phi = 1 + \frac{k_1}{k_F + k_{nr}} \, \frac{k_2 + k_{30} - a[Q]}{k_{-10} + k_2 + k_{30} + (b-a)[Q]}[Q] .$$

In non polar solvents, such as aliphatic hydrocarbons, the addition of non polar quenchers (e.g. CCl_4) does not significantly lower the electric permeability of the mixture [23]: k_{-1} and k_3 are practically constant. ϕ_0/ϕ should obey a Stern-Volmer relation over the whole concentration range of the quencher. A similar mechanism has been suggested by Murata [24] for the fluorescence quenching of 2-ethoxynaphthalene by methyl benzoate in dimethylformamide and cyclohexane.

The parabolic shape of the fluorescence quenching curves in mixtures of CCl_4 with solvents of low polarity (benzene, methylbenzene, ethers and esters) we interpreted in paper I [12] as an effect of a specific interaction of the electron-donor-acceptor type of the solvent with the CCl_4. Such interactions have been well documented [25 – 34].

Here we propose the above second mechanism as an alternative, especially for solvents with high polarity. In general, the fluorescence quenching of aromatic hydrocarbons may proceed according to both mechanisms. The contribution of either of them to the total quenching may vary in different solvents and its share is difficult to estimate.

The influence of intermolecular interactions between CCl_4 and a mixture component on the fluorescence of aromatic hydrocarbons suggests to exploit the hydrocarbons as luminescent probes monitoring such interactions.

Acknowledgement

Our thanks are due to Professor Dr. Z. R. Grabowski, Institute of Physical Chemistry, Polish Academy of Sciences, for providing facilities for carrying out the measurements of the fluorescence decay curves and to Dr. J. Sepioł from that Institute for his assistance in the measurements. We are much indebted to Professor A. Schmiller, Giessen, for many helpful discussions and critical reading of the manuscript.

[1] H. W. Melhuish and W. S. Metcalf, J. Chem. Soc. A. **1954**, 967; H. W. Melhusih and W. S. Metcalf. J. Chem. Soc. **1958**, 480.

[2] E. J. Bowen and W. S. Metcalf, Proc. Roy. Soc. London **A 206**, 437 (1951).

[3] M. V. Encinas, M. A. Rubio, and E. A. Lissi, J. Photochem. **18**, 137 (1982).

[4] N. Solvarajan, M. M. Panicker, S. Vaidyanathan, and V. Ramakrishnan, Indian J. Chem. **18 A**, 23 (1979).

[5] D. Schulte-Frohlinde and R. Pfefferkorn, Ber. Bunsenges. Phys. Chem. **72**, 330 (1968).

[6] E. J. Bowen and J. Sahu, J. Phys. Chem. **63**, 4 (1959).

[7] S. Ander, G. Heinrich, and D. Schulte-Frohlinde, J. Chem. Soc. Chem. Comm. **1968**, 745.

[8] G. Kallman-Oster, Acta Phys. Polon. **26**, 435 (1964).

[9] E. J. Bowen and K. K. Rohatgi, Disc. Faraday Soc. **14**, 146 (1953).

[10] G. Vermeerch, J. Marko, N. Febvay-Garet, S. Caplain, and V. Lablanche-Combier, Tetrahedron **34**, 1439 (1978).

[11] C. Lewis and W. R. Ware, Chem. Phys. Lett. **15**, 290 (1972); W. R. Ware and C. Lewis, J. Chem. Phys. **57**, 3546 (1972).

[12] W. M. Wiczk and T. Latowski, Z. Naturforsch. **41 a**, 761 (1986).

[13] J. Jasny, J. Luminescence **17**, 149 (1978).

[14] J. N. Demas and G. A. Crosby, J. Phys. Chem. **78**, 991 (1971).

[15] J. N. Demas and G. A. Crosby, Anal. Chem. **42**, 1010 (1979); N. J. Greer, F. N. Reed, and J. N. Demas, ibid. **53**, 710 (1981); J. Y. Jerequel, M. Bouchy, and J. C. André, ibid. **54**, 2199 (1982).

[16] L. K. Patterson, G. Porter, and M. R. Topp, Chem. Phys. Lett. **7**, 612 (1970).

[17] B. Stevens and B. E. Algar, J. Phys. Chem. **72**, 2582 (1968).

[18] S. L. Murov, Handbook of Photochemistry, Marcel Dekker Inc., New York 1973, p 89.

[19] J. L. Kropp, W. R. Dawson, and M. W. Windsor, J. Phys. Chem. **73**, 1747 (1969).

[20] A. R. Watkins, Chem. Phys. Lett. **65**, 380 (1979).

[21] J. F. Coetzee and I. M. Kolthoff, J. Amer. Chem. Soc. **79**, 6110 (1957).

[22] W. R. Ware, J. Phys. Chem. **66**, 455 (1962).

[23] Poradnik Fizykochemiczny, WNT Warszawa 1974, p B-110; Ya. Yu. Ahabov, Dielectric properties of two-component mixtures of solvents, Nauka 1977 (in Russian).

[24] I. S. Murata, J. Photochem. **14**, 167 (1980).

[25] D. R. Rosseinsky and H. Kellawi, J. Chem. Soc. A. **1969**, 1207.

[26] D. A. Bahnick and W. B. Person, J. Chem. Phys. **48**, 1252 (1968).

[27] W. F. Murphy, M. V. Evans, and P. Bonder, J. Chem. Phys. **47**, 1836 (1968).

[28] R. Mierzecki, J. Mol. Structure, **47**, 53 (1978).

[29] R. P. Rastogi, J. Nath, and R. B. Yadawa, Indian J. Chem. **8**, 541 (1970).

[30] M. D. Gullen, S. Otin, M. Gracia, and C. Gutierez-Losa, J. Chim. Phys. **72**, 425 (1975).

[31] H. Kehaian, Bull. Acad. Polon. Sc. Ser. Chim. **11**, 583 (1963).

[32] D. P. Erap and S. Glastone, J. Chem. Soc. **1935**, 1720.

[33] G. Kozakowski and R. Mierzecki, Polish J. Chem. **53**, 947 (1979).

[34] Z. Kecki, Spectrochim. Acta **18**, 1155, 1165 (1962).