Fluorescence Investigations on Intramolecular Energy Transfer in Alkyl-Fluorenole and Alkyl-Anthracene

E. Fick, H. Herler, and H. Heusinger
Institut für Radiochemie der Technischen Universität München, Garching bei München

(Z. Naturforsch. **26 a**, 794—798 [1971]; received 9 February 1971)

Herrn Professor Dr. Nikolaus Riehl zum 70. Geburtstag gewidmet

Fluorescence investigations of alkyl fluorenole- and alkyl anthracene-solutions in *n*-hexane or cyclohexane resp. were performed for β- and UV-excitation. The observed influence of scavengers for electrons or positive ions on the fluorescence intensity for β-excitation reveals that charge transfer is the predominant process for the intermolecular energy transfer from solvent to solute.

The fluorescence intensity of alkyl fluorenoles and alkyl anthracenes increases with increasing number n of CH_2-groups in the alkyl chain, reaching a plateau for $n \sim 6$. This gives evidence for intramolecular energy transfer within the CH_2-chain with a limited range. Using a simple model in alkyl fluorenoles for the transfer probability from C_n to C_{n-1} in the chain a value of 0.65 could be deduced. The model derived for *n*-alkyl fluorenoles fits to the values of branched alkyl fluorenoles as well.

The results obtained from the fluorescence measurements are compared with those on C—H-bond breakage in the aliphatic chain, derived from investigations of hydrogen production and radical formation. Possible mechanisms for intramolecular energy transfer are discussed.

Already small concentrations of aromatic compounds reduce the radiolytic product formation of alkanes very effectively [1]. On the other hand, for excitation with ionizing radiation the fluorescence efficiency of dilute solutions of aromatic compounds in aliphatic hydrocarbons is much larger than expected from the energy absorbed by the aromatic solute. These effects are explained by intermolecular energy transfer.

Intramolecular energy transfer in aliphatic CH_2-chains is often invoked to explain the fact that an especially effective radiation protection is observed if aromatic groups are bond to aliphatic chains. If there exists intramolecular energy transfer from the aliphatic chain to the aromatic group, the reduction in product formation in the aliphatic part should correspond to an increase in reactions characteristic for the aromatic part. Due to the radiation stability of aromatic groups, this is difficult to test by chemical product formation, although there exists some evidence for such a relation from product formation [2] and ESR-spectroscopy [3, 4]. For aromatic compounds, their ability to fluoresce is characteristic. The aim of this work was to test, if there exists a correlation in alkyl aromatic compounds between radiolytic product formation in the aliphatic chain and radiation induced fluorescence.

Experimental

Fluorescence Measurement

For β-excitation a 2 mCi Kr^{85} source in a nickel tubule was used. Kr^{85} is a weak β-emitter with 0.67 MeV energy.

Reprints request to Dr. H. Heusinger, Institut für Radiochemie der Technischen Universität München, *D-8046 Garching* bei München.

The apparatus for determination of the relative fluorescence intensities is shown in Fig. 1.

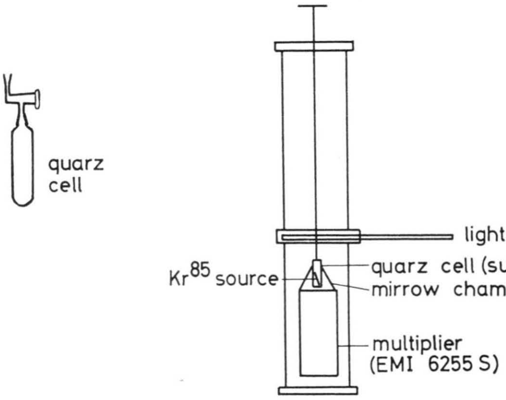


Fig. 1. Experimental arrangement for determination of the relative fluorescence intensities for β-excitation.

The fluorescence spectra and relative quantum efficiencies for UV excitation were determined by a Zeiss fluorescence spectrometer with two monochromators.

The fluorescence maxima for β-excitation were determined by immersing the Kr-source in the quartz cell of the fluorescence spectrometer.

---

[1] J. P. Manion and M. Burton, J. Phys. Chem. **56**, 560 [1952].
[2] M. Burton and N. Patrick, J. Phys. Chem. **58**, 421 [1954].
[3] A. Zeman and H. Heusinger, J. Phys. Chem. **70**, 3374 [1966]; Radiochim. Acta **8**, 149 [1967].
[4] I. Kules and M. Erö-Gécs, Acta Chim. Acad. Sci. Hung. **58**, 389 [1968].

Materials

n-Hexane and cyclohexane (Merck) and anthracene (Schuchardt) for spectroscopy were used without purification.

Fluorenole was produced by reduction of fluorenone. It was purified by recristallisation from benzene or alcohol.

Methyl-, ethyl- and propyl-fluorenole were prepared from fluorenone by Grignard syntheses. The alkyl fluorenoles with larger chain length were prepared by a method given by SWAIN and BOYLES [5] adding $MgBr_2$ to the Grignard solution. This addition of a Lewis acid inhibits Gignard reduction in the presence of voluminous reactants. The compounds were purified on a silica gel column in alcoholic solution and recristallized from methanol. Traces of the solvent were removed by evacuation. Melting points of the purified compounds: fluorenole 159 °C, methyl-fluorenole 174 °C, ethyl-fluorenole 102 °C, propyl-fluorenole 125 °C, amyl-fluorenole 132 °C, isopropyl-fluorenole 124 °C, nonyl-fluorenole 136 °C.

Alkyl anthracenes were prepares by Gignard synthesis from anthracene by a method described by KROLLPEIFFER and BRANDSCHEID [6].

Sample Preparation

The quartz cell (see Fig. 1) containing the ^{85}Kr-source was filled with 2 ml of scintillator solution. The solutions were degased in a high vacuum apparatus by three freeze (77 °K) pump, thaw cycles. In the case of anthracene solutions care was taken not to expose them to light.

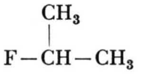
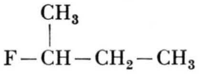
Results

The relative fluorescence intensity of anthracene in dependence on solute concentration for β- and UV-excitation is shown in Fig. 2.

The influence of electron scavengers – CCl_4, C_6F_{12}, C_2H_5Br, $\Phi\text{-}NO_2$, $CH_3-COOCH_2-\Phi$ – and of piperidine, a scavenger for positive ions is shown in Fig. 3 and 4 for β- and UV-excitation.

For β-excitation in Fig. 5 the dependence of the fluorescence intensity on the number n of CH_2-groups in the aliphatic chain is plotted for alkyl fluorenoles and alkyl antracenes. Tab. 1 gives some values for isomeric alkyl fluorenoles.

Table 1. Fluorescence intensities of isomeric alkyl fluorenoles.

	rel. fluorescence intensity
 $F-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$	2.645
 $F-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$	2.845

The values given in Fig. 5 and Tab. 1 are corrected for the relative fluorescence quantum efficiency, determined by UV-excitation. The quantum efficiencies of the alkyl compounds differ only

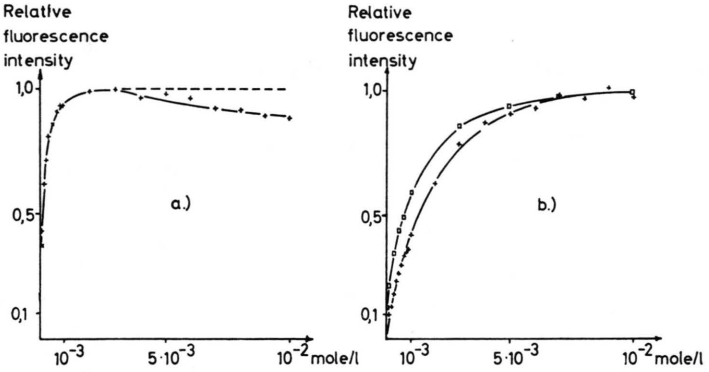


Fig. 2. Fluorescence intensity in dependence of solute concentration. a) UV-excitation $\lambda_{\text{excitation}}=357$ nm; layer thickness: 10 mm. + anthracene in cyclohexane; – – – – calculated by the equation $I_{\text{rel}} \sim 1-e^{-c}$. b) β-excitation, —+— anthracene in cyclohexane, —□— anthracene in hexane.

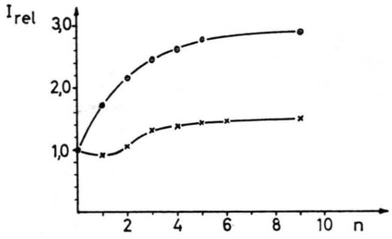


Fig. 3. Influence of electron scavengers on the fluorescence intensity 10^{-3} mole/l anthracene in cyclohexane.

	β-excitation	UV-excitation ($\lambda_{\text{exc}}=357$ nm)
CCl_4	△	▲
C_6F_{12}	□	■
C_2H_5Br	○	●
$Ø-NO_2$	▽	▼
$CH_3-COOCH_2-Ø$	⛉	⛊

---

[5] C. G. SWAIN and H. R. BOYLES, J. Amer. Chem. Soc. **73**, 870 [1951].

[6] F. KROLLPFEIFFER and F. BRANSCHEID, Ber. **56**, 1618 [1923].

slightly, larger changes are observed between the pure aromate and the alkyl compounds. For β-excitation, due to the low light intensity, the fluorescence spectrum was not well resolved, but it could be shown, that the fluorescence maximum does not differ from the UV-excatation maximum.

Discussion

By UV-excitation the aromatic solute molecules are excited directly. In the investigated concentration range for the light absorption the validity of Lambert-Beers law can be presumed. The fluorescence intensity as a function of solute concentration c therefore should be given by

$$I_F = \Phi\, F\, I_0 (1 - e^{-\varepsilon c d}) ,$$

I_F = fluorescence intensity, I_0 = intensity of exciting light, Φ = quantum efficiency, F = geometric factor of the experimental arrangement, ε = molar extinction coefficient, c = concentration of scintillator, d = layer thickness.

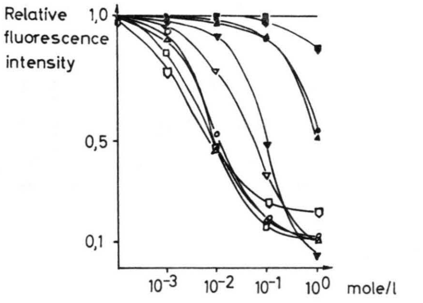


Fig. 4. Influence of piperidine on the fluorescence intensity 10^{-3} mole/l anthracene in cyclohexane.
☐ β-excitation; ■ UV-excitation (λ_{exc} = 357 nm).

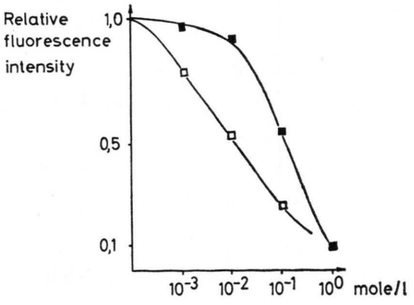


Fig. 5. Fluorescence intensity I_{rel} as a function of the number of CH_2-groups in the alkyl chain.
⊙ alkyl fluorenoles; × alkyl anthracenes.

For anthracene solutions (Fig. 2 a) the experimental values are in agreement with this relation up till about 3×10^{-3} mole/l. For concentrations $> 3 \times 10^{-3}$ mole/l deviations are observed. Self-absorption cannot be responsible for these deviations, because the fluorescence peak at 23500 cm^{-1}, which does not overlap with the absorption spectrum, shows the same dependence as the main peak at 25000 cm^{-1}. This effect will be due to concentration quenching originating in the formation of non fluorescent dimers[7].

For β-excitation in the investigated concentration range (10^{-2} mole/l anthracene corresponds to an electron fraction of $1{,}9 \times 10^{-3}$) energy is absorbed by the solvent and direct excitation of the solute can be ignored. Fluorescence originates from excited solute molecules.

These excited states must be produced by energy transfer from solvent molecules. Fig. 2 b shows, that the fluorescence intensity reaches a limiting value for solute concentrations $> 10^{-2}$ mole/l. From the observed concentration dependence an approximate range for this intermolecular energy transfer from the solvent to the solute can be deduced using a simple model:

We presuppose a homogeneous distribution of aromatic molecules in the solvent and the diffusion of the solute molecules and of the primary species in the solvent during their lifetime is neglected. A volume $v = 4/3\, \pi R^3_{\text{w}}$ with radius R_{w} around the primary excited or ionized solvent molecule is so defined, that energy transfer to a solute molecule within this volume takes place with certainty, while energy transfer to solute molecules outside this volume is impossible. This simplification implies that fluorescence is only observed from solute molecules within a distance R_{w} around the absorbing solvent molecule. Calculation of the probability to find one or more solute molecules within this distance as a function of solute concentration leads to the following expression for the fluorescence intensity[8]

$$I/I' = I_{\text{rel}} = 1 - e^{-(v/V)N} = 1 - e^{-v c N_L} ,$$

I = fluorescence intensity, I' = fluorescence intensity for infinite concentration (corrected for concentration quenching), $v = \frac{4}{3} \pi R_{\text{w}}^3$ = sensitive volume, V = sample volume, $N = V\, c\, N_L$ = number of solute molecules in V, c = concentration of solute [mole/l].

---

[7] A. Dammers-de Klerk, Mol. Phys. **1**, 141 [1958].

[8] For a detailed derivation compare J. Wilske and H. Heusinger, J. Pol. Sci. A 1, **7**, 995 [1969] and literature cited there.

Based on this equation from the experimental results a R_w of 58 Å for anthracene in cyclohexane and of 60,4 Å for anthracene in n-hexane is obtained.

While for UV-excitation excited states of the solute are directly formed for β-excitation a large part of the primary species produced in the solvent are ions and electrons. In order to get information on the participation of these charged species in the intermolecular energy transfer from the solvent to the solute the influence of electron scavengers and piperidine, a scavenger for positive ions, on the fluorescence intensity of anthracene solutions was investigated (Fig. 3 and 4).

Starting from the primary ions (RH^+, e) the following reactions have to be discussed for the fluorescence emission by anthracene (A).

$$RH^+ + A \rightarrow RH + A^+ , \qquad (1)$$

$$e + A \rightarrow A^- , \qquad (2)$$

$$A^+ + e \rightarrow A^* \rightarrow h\nu , \qquad (3)$$

$$A^+ + A^- \rightarrow A^* + A \rightarrow h\nu , \qquad (4)$$

$$RH^+ + A^- \left\{ \begin{array}{ll} \rightarrow RH^* + A & (5\,a) \\ \quad \downarrow & \\ \quad \text{Prod} & \\ \rightarrow RH + A^* & (5\,b) \\ \qquad\quad \downarrow & \\ \qquad\quad h\nu & \end{array} \right.$$

in presence of an electron scavenger

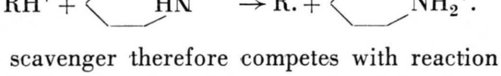
$$e + F \rightarrow F^- , \qquad (6)$$

$$A^+ + F^- \mathrel{-\!\|\!\!\rightarrow} h\nu , \qquad (7)$$

$$RH^+ + F^- \rightarrow \text{Prod.} \qquad (8)$$

In this system, charge transfer (reaction 1) and electron scavenging (reaction 2) are in competition with geminate ion-electron recombination in the solvent. An electron scavenger competes for electrons with anthracene (reaction 2 and 6), and reaction 4 and 5 b are replaced by the corresponding reactions of the scavenger anions (reaction 7 and 8). Due to the large electron affinity of the scavengers, the charge recombination of an anthracene ion with an scavenger anion (reaction 7) will not produce fluorescence.

Piperidine is known to give proton transfer with alkane molecular ions



This scavenger therefore competes with reaction 1 and 5. Reaction 3 and 4 are replaced by the corresponding charge recombination with the scavenger ion, which does not produce fluorescence.

A comparison of the results for UV- and β-excitations in Fig. 3 and 4 shown that the very effective reduction in fluorescence intensity by the scavengers for β-excitation cannot be due to quenching of excited states. This effect is plausible, if for excitation with ionizing radiation charge transfer from solvent ions to solute molecules is of importance for the fluorescence. This result is in agreement with a recent publication by HENTZ and KNIGHT [9], who investigated the influence of electron scavengers on the fluorescence efficiency of terphenyl solutions.

As shown in Fig. 5 the fluorescence intensity of β-excited alkyl fluorenole solutions increases with the number n of CH_2-groups in the aliphatic chain reaching a plateau for $n \sim 6$. This effect can be understood if intramolecular energy transfer to the aromatic group in the alkyl chain bond chemically to it is more effective than intermolecular energy transfer via solvent molecules.

A quantitative evaluation was performed for alkyl fluorenoles. The experiments with scavengers for electrons and positive charge showed, that for intermolecular energy transfer from the solvent to the solute primarily charge transfer is responsible. We assume that in alkyl fluorenoles charge can be transferred either directly to the aromatic group or to the aliphatic chain, from where it is transferred intramolecularly to the aromatic group:

$$RH^{\ddagger} + F-(CH_2)_nH \left\langle \begin{array}{l} \rightarrow RH \qquad\qquad + F^{\ddagger}-(CH_2)_nH \\ \qquad\qquad\qquad\qquad\qquad \uparrow \\ \rightarrow RH + F-(CH_2)_n{}^{\ddagger}H \;\text{—} \\ \qquad\qquad\qquad \text{intramolecular} \end{array} \right.$$

The fluorescence intensity then can be described by

$$I_{F(CH_2)_nH} = I_{\text{direct}} + I_{\text{intra}} .$$

If we suppose that on the average any CH_2-group of the alkyl chain takes up the same amount of energy E, the contribution of intramolecular transfer is determined by two quantities

$$F \xleftarrow{p} \underset{1}{CH_2} \xleftarrow{q} \underset{2}{CH_2} \xleftarrow{q} \underset{3}{CH_2} \xleftarrow{q} \underset{4}{CH_2} - \underset{n}{\ldots} ;$$

p = transfer probability from C_1 to fluorenole for this probability we just assume, that it is constant for all alkyl fluorenoles; q = propability for energy transfer within the chain from C_n to C_{n-1}.

---

[9] R. HENTZ and J. KNIGHT, J. Phys. Chem. **72**, 1783 [1968].

The contribution of intramolecular energy transfer to fluorenole as a function of the number n of CH_2-groups in the alkyl chain will be:

$$\begin{array}{ll} F-(CH_2)H & pE\,, \\ F-(CH_2)_2H & p(E+E\,q)\,, \\ F-(CH_2)_nH & p\,E\sum\limits_{v=1}^{v=n} q^{v-1}\,. \end{array}$$

The energy difference of two consecutive members with $(CH_2)_n$ and $(CH_2)_{n-1}$ will be given by

$$E_{F(CH_2)\;H} - E_{F(CH_2)_{n-1}H} = p\,E\,q^{n-1}\,.$$

The measured fluorescence intensities (I) are proportional to these energies. In order to eliminate the unknown quantities p and E the ratio is formed

$$\frac{E_{F(CH_2)_nH} - E_{F(CH_2)_{n-1}H}}{E_{F(CH_2)\;H}} = \frac{I_n - I_{n-1}}{I_{n=1} - I_{n=0}} = q^{n-1}$$

or

$$\frac{I_n - I_{n-1}}{\log I_{n=1} - I_{n=0}} = \log q\,(n-1)\,.$$

From this equation a value for q of $0{,}65 \pm 0{,}08$ is deduced using the experimental realtive fluorescence intensities.

This simple model also fits to the investigated alkyl fluorenoles with branched chains. In Tab. 2 the values calculated on the basis of the model are compared with the experimental results.

Table 2. Comparison of experimental results obtained for branched alkyl chains with values calculated on the basis of the model.

		change in fluorescence intensity calcul.	experim.
$(F-C_1-C_2)-(F-C_1)$	$\triangleq E\,q$		0.475
$(F-\overset{C_{2b}}{\overset{\vert}{C_1}}-C_{2a})-(F-C_1)$	$\triangleq 2\,E\,q$	0.950	0.965
$(F-C_1-C_2-C_3)-(F-C_1)$	$\triangleq E\,q+E\,q^2$	0.783	0.790
$(F-\overset{C_{2b}}{\overset{\vert}{C}}-C_{2a}-C_3)-(F-C_1)$	$\triangleq 2\,E\,q+E\,q^2$	1.150	1.165

In alkyl anthracenes the observed increase in fluorescence intensity with increasing chain length for $n>2$ also gives evidence for intramolecular energy transfer with a limited range of about 6 CH_2-groups. It can be described by the model derived for alkyl fluorenoles. But the first two members in alkyl anthracenes obviously do not fit in the model.

A comparison of the results obtained from fluorescence measurements with those obtained from chemical product formation in alkyl aromatic compounds reveals that there is a strong correlation. So, in alkyl-benzenes[3] and diphenyl-alkanes[4] the protection on hydrogen production shows a limited range of $5-6$ CH_2-groups. ESR-investigations also reveal a protection of the alkyl part by the aromatic group on radical formation. This protection decreases with increasing alkyl chain[3, 4].

For intramolecular energy transfer, charge transfer or excitation transfer have to be discussed. Both processes predict migration predominantly along the molecular chain. They are difficult to distinguish by experiment. From fluorescence investigations of alkyl aromatic compounds in presence of electron scavengers, no conclusions on the mechanism of intramolecular transfer could be drawn, because the intermolecular charge transfer process from solvent to solute is suppressed by these scavengers.

To explain the correlation of fluorescence intensity and C – H-bond breakage in alkyl aromatic compounds in the case of intramolecular charge transfer, ion electron recombination and ion dissoziation in the aliphatic chain should be in competition with charge transfer to the aromatic group.

On the other hand, for long chain alkanes based on vacuum UV-absorption spectroscopy two exciton bands are discussed[10, 11], a migratory C – C-band and a localized C – H-band. The limited range of intramolecular energy transfer derived from fluorescence measurements and reactions originating in C – H-bond breakage can be explained from this point of view by a mixing of the localised C – H-band with the migratory C – C-band in the vicinity of the acceptor molecule. Part of the energy localized in a CH-bond in a pure alkane, will be able to migrate to the aromatic acceptor in an alkyl aromatic compound.

Acknowledgements

The authors wish to thank Prof. Dr. H.-J. BORN for his constant interest in this work. We further thank the Deutsche Forschungsgemeinschft and the Bundesministerium für Wissenschaftliche Forschung for their support.

---

[10] J. W. RAYMONDA and W. T. SIMPSON, J. Chem. Phys. **47**, 430 [1967].

[11] W. F. LOUVIER and W. H. HAMILL, J. Phys. Chem. **72**, 3878 [1968].