







Diffusion

$$k_{DIF} = \frac{8RT}{3000\eta}$$

η is the viscosity of the solvent (in units of Poise, P) *R* is the gas constant (8.31 x 10⁷ erg/mol or 1.99 cal mol⁻¹ K⁻¹).

For typical non-viscous organic solvents (benzene, acetonitrile, hexane) at room temperature η is ~ 1-10 cP

 k_{DIF} has a value of around 10⁹-10¹⁰ M⁻¹s⁻¹.





Mechanisms

Radiative Energy Transfer

• Trivial ET

- Non-Radiative Energy Transfer
 - Resonance ET
 - Exchange ET



 $*D \longrightarrow D + hv$ $hv + A \longrightarrow *A$

Depends On:

- + The quantum yield ($\Phi_{e}^{\rm D}$) of emission of *D
- The number of A molecules (concentration) in the path of photons emitted by *D
- + The light absorbing ability (extinction coefficient, $\epsilon_{A})$ of A
- The overlap of the emission spectrum of *D and the absorption spectrum of A, with consideration given to the extinction coefficient, ε_{A} , of A at the wavelength of overlap.



















A bit of history: Glass at 77° K to Solution at RT Phosphorescence and the triplet state G. N. Lewis and M. Kasha. J. Am. Chem. Soc. 63. 3005. 1941 Sensitized phosphorescence of aromatic compounds A. N. Terenin and V. Ermolaev, Doklady, Acad. Sc., U.S.S.R., 85, 547, 1952 Sensitized phosphorescence in organic solutions at low temperature: Energy transfer between triplet states A. N. Terenin and V. Ermolaev, Trans. Faraday Soc., 52, 1042, 1956 Quenching of biacetyl fluorescence in solution H. L. J. Backstrom and K. Sandros, J. Chem. Phys. 1955, 2197 The quenching of long-lived fluorescence of biacetyl in solution H. L. J. Backstrom and K. Sandros, Acta Chemica Scand. 1958, 12, 823 Transfer of triplet state energy in fluid solution: Sensitized Phopshorescence and its application to the determination of triplet state lifetimes H. L. J. Backstrom and K. Sandros, Acta Chemica Scand. 1960, 14, 48 Energy transfer from the triplet state G. Porter and F. Wilkinson, Proc. Royal Soc. A, 1961, 264, 1



















Sensitizers

- > Should be able to excite the sensitizer alone even in presence of acceptor.
- \succ Sensitizer should have high intersystem crossing efficiency (S1 to T1).
- > Sensitizer should have triplet energy higher than the acceptor.
- > Sensitizer should be photostable.



	Es	ET	TS	τ _T		
Compound	(kcal mol ⁻¹)		(s)		Conf. T ₁	Φ_{ST}
Benzene	110	84	$\sim 10^{-7}$	10-6	π.π*	0.2
Acetone	~ 85	~ 78	10-9	10-5	n. π *	1.0
Xanthone		74			π.π*	1.0
Acetophenone	~ 79	74	10-10	10-4	n. 	1.0
4-CF3Acetophenone		71			n. π *	1.0
Benzophenone	~75	69	10-11	10-4	n,π*	1.0
Triphenylene	83	67	$\sim 5 \times 10^{-8}$	10-4	π.π*	0.9
Thioxanthone	78	~ 65				
Anthraquinone		62			n,π*	1.0
4-Ph-benzophenone	77	61		10^{-4}	π,π*	1.0
Michler's ketone		61				1.0
Napthalene	92	61	10-7	10^{-4}	π,π*	0.7
2-Acetonaphthalene	78	59		10-4	π.π*	1.0
1-Acetonaphthalene	76	57		10-4	π,π*	1.0
Chrysene	79	57	5×10^{-8}		π.π*	0.8
Biacetyl	~ 60	55	10-8	10^{-3}	n, π *	1.0
Benzil	~ 59	54	$\sim 10^{-8}$	10-4	n,π*	1.0
Camphorquinone	~ 55	50	$\sim 10^{-8}$		n,π*	1.0
Pyrene	77	49	$\sim 10^{-6}$		π,π*	0.3
Anthracene	76	47	$\sim 5 \times 10^{-9}$	10^{-4}	π,π*	0.7
9,10-Dichloroanthracene	~ 74	40	$\sim 5 \times 10^{-9}$	10^{-4}	π,π*	0.5
Perylene	66	~ 35	5×10^{-9}		π.π*	0.00











































E and P-Type Delayed Fluorescence

Anthracene, Phenanthrene, Naphthalene, Benzpyrene etc.

CA Parker & CG Hatchard, *Proc. Chem. Soc.*, **1962**, 147 CA Parker & CG Hatchard, *Proc. R. Soc. London. Ser.A.* **1962**, 269, 574 CA Parker & CG Hatchard, Nature, **1963**, 200, 331

"The intensity of the emission is proportional to the square of the rate of light absorption."

Pyrene CA Parker & CG Hatchard, Trans. Faraday Soc., 1963, 59, 284

"The delayed fluorescence produced by triplet-triplet quenching is sharply different from that of eosin. To facilitate distinction between the two types we suggest the one be called E-type (eosin) and the other P-type (pyrene)."









			Total spin	Arrow	Multipilicity	Name of final
T _n	T _n	T _n	$S = T_n + T_n$	notation	= (2S + 1)	state, Symbol
Case 1	$T_{*1}(\uparrow\uparrow)$	T ₋₁ (↓↓)	0	ţîţ	1	Singlet, S
Case 2	$T_{+1} (\uparrow\uparrow)$	$T_0(\downarrow\uparrow)$	+1	↑↑↓↑	3	Triplet, T
Case 3	T ₊₁ (↑↑)	T ₊₁ (↑↑)	+2	1111	5	Quintet, Q

Properties of TTA in Solution Direct light absorption

- The rate constants for TTA, ktta, are generally very large.
- With laser light excitation, triplet state concentrations in excess of 10⁻⁵ M can be readily achieved. Typical products $k_{TTA}[D^*(T_1)]$ may then be around or over 10^5 s⁻¹. Thus, any triplet with lifetime of a few microseconds (a common situation) will undergo at least some TTA in fluid solution.
- The high sensitivity with which fluorescence can be detected makes TTA an easily observable process even when it is not the major mechanism for triplet decay.













Selected Reviews

C. A. Parker, Phosphorescence and Delayed Fluorescence from Solutions, Adv. Photochem., **1964**, *2*, 305

Photon upconversion based on sensitized triplet–triplet annihilation, T. N. Singh-Rachford, F. N. Castellano, Coordination Chemistry Reviews, **2010**, *254*, 2560–2573

C. E. McCusker, F. N. Castellano, Materials Integrating Photochemical Upconversion, Top Curr Chem (Z) **2016**, 374, 19

Upconversion Luminescent Materials: Advances and Applications J. Zhou, Q. Liu, W. Feng, Y. Sun, and F. Li, Chem. Rev. **2015**, *115*, 395

New perspectives for triplet–triplet annihilation based photon upconversion using all-organic energy donor & acceptor chromophores, A. Jean-Luc Ayitou et. al., Chem. Commun., **2018**, *54*, 5809.









¹O₂ sensitizers (singlet)

Rate constants and singlet oxygen efficiencies from excited singlets by oxygen

Solvent	(S∆ ^s)a	k _q ^S , 10 ⁹ (M-1s-1)
Acetonitrile	≤ 0.09	31
Acetonitrile	0	33
Acetonitrile	≤ 0.02	37
Acetonitrile	0.30	29
Acetonitrile	0.30	6.6
Acetonitrile	0.27	38
Acetonitrile	0.25	42
Acetonitrile	≤ 0.02	30
	Solvent Acetonitrile Acetonitrile Acetonitrile Acetonitrile Acetonitrile Acetonitrile Acetonitrile Acetonitrile	Solvent $(S\Delta^s)a$ Acetonitrile ≤ 0.09 Acetonitrile0Acetonitrile ≤ 0.02 Acetonitrile 0.30 Acetonitrile 0.27 Acetonitrile 0.25 Acetonitrile ≤ 0.02

For the ET to be effective the singlet-triplet (S_1-T_1) energy gap of the donor must be greater than the energy gap between the ground and singlet state of oxygen (22.4 kcal/mol), the acceptor.

The π,π^* triplet states of polynuclear aromatics are generally highly efficient at producing singlet oxygen, frequently with $S\Delta \geq 0.8$. The n,π^* triplet states of ketones have low values of $S\Delta$, for example for benzophenone $S\Delta$ is in the 0.3-0.4 range. Depends on the S_1 – T_1 gap.







Contemporary Skepticism G. O. Schenck

'Sens--OO' (moloxide)

Papers on photooxidation were one-sided Photooxidation attributed to sensitizer—oxygen adduct Many discounted the contribution of ${}^{1}O_{2}$ (${}^{1}\Delta_{o}$)



References:

Schenck, G. O. Naturwiss. **1948**, 35, 28 Blum, H. F. *Physiol. Rev.* **1945**, 25, 483 Bowen, E. J. *Discussions Faraday* Soc. **1953**, 14, 143 Terenin, A. N. *Akad. Nauk* S.S.S.R. **1955**, 85 Livingston, R. S. *Conf. Biol. Antioxidants Trans.* **1950**, 5, 17



G. O. Schenck (1913-2003)

Sens--OO (moloxide) GO. Schenck, G. O. *Naturwiss.* 1948, 35, 28 Singlet Oxygen

Foote, C. S.; Wexler, S. J. Am. Chem. Soc. **1964**, 86, 3879 Foote, C. S.; Wexler, S. J. Am. Chem. Soc. **1964**, 86, 3880 Wolf, ; Foote, C. S.; Rebek, J. J. Am. Chem. Soc. **1978**, 100, 7770

 ${}^{1}\Sigma_{g}^{+}$ Singlet Oxygen as the reactive species

H. Kautsky et. al., Naturwissenschaften, 1931, 19,1043

H.Kautsky, et. al., Dtsch. Chem. Ges., 1933, 66, 1588.

H. Kautsky, Biochem. Z, 1937, 291,271(1937)

H. Kautsky, Trans. Faraday Soc., 1939, 35, 216.



H. Kautsky G. O. Schenck



C. S. Foote



Plants that commonly grow in the shade benefit from having a variety of light-absorbing pigments. Each pigment can absorb different wavelengths of light, which allows the plant to absorb any light that passes through the taller trees.



Singlet Oxygen









History singlet-singlet energy transfer

Hg vapor to Na or Tl vapor G. Cario and J. Franck, Z. Physik, 17, 202 (1923).

Hg vapor to H_2 Xe vapor to H_2 H. Calvert, Z. Physik, 78, 479 (1932)

Anthracene to Naphthalene crystals A. Winterstein and K. Schon, Naturwiss., 22, 237 (1934) E. J. Bowen, Nature, 142, 108 (1938)

Tryptaflavin to Rhodamine B in solution (> 70Å) T. Forster, Z. Elektrochem., 63, 93 (1949)

1-Chloroanthracene to perylene E. J. Bowen and B. Brocklehurst, Trans. Faraday Soc., 49, 1131 (1953)

Milestones in the Theory of Resonance Energy Transfer

1918 J. Perrin proposed the mechanism of resonance energy transfer. A theoretical interpretation of energy transfer between molecules, involved fluorescence polarization in a solution of a single chemical species of fluorophore.

1922 G. Cario and J. Franck demonstrate that excitation of a mixture of mercury and thallium atomic vapors with 254nm (the mercury resonance line) also displayed thallium (sensitized) emission at 535nm.

1928 H. Kallmann and F. London developed the quantum theory of resonance energy transfer between various atoms in the gas phase. The dipole-dipole interaction and the parameter R_0 were used for the first time.

1932 F. Perrin published a quantum mechanical theory of energy transfer between molecules of the same specie in solution. Qualitative discussion of the effect of the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.

1941 W. Arnold and J.R. Oppenheimer, published an abstract on FRET during photosynthesis process and full article in 1950

1946-1949 T. Förster developed the first quantitative theory of molecular resonance energy transfer.



Förster formulation						
$k_{\rm ET} \left(\text{dipole} - \text{dipole} \right) = \alpha \frac{\kappa^2 k_D^{\circ}}{R_{DA}^6} J\left(\varepsilon_{\Lambda} \right)$						
$k_{ET} = \frac{\phi_D \kappa^2}{\tau_D r^6} \frac{9000 \ln 10}{128\pi^5 N_A n^4} \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$						
ϕ_D : Fluorescence quantum yield of donor in absence of acceptor						
κ^2 : Orientation factor						
τ_D : Lifetime of donor in absence of acceptor						
r : Donor – acceptor distance						
NA: Avogadro number						
n : Refractive index of the medium						
$F_D(\lambda)$: Normalized fluorescence spectrum of donor						
$\varepsilon_A(\lambda)$: Normalized absorption spectrum of acceptor						

Förster Resonance Energy Transfer from excited donor to ground state acceptor depends on:

Spectral overlap

Distance

Alignment (Orientation)















Dipole-dipole mechanism will be most favored for *D and A pairs such that:

- The *D \rightarrow D and A \rightarrow *A processes correspond to a large (spectral) overlap integral, *J*.
- The radiative rate constant, k°_{D} , is as large as possible.
- The magnitude of ε_A is as large as possible.
- There is a small spatial separation between *D and A.
- There will be a preferred orientation for which energy transfer is most favorable.













mapping of proteins,	and their values of R_0 :	i ili sciucturai
Donor	Acceptor	R _o [Å]
Fluorescein **	Tetmethylrhodamine	55
IAEDANS	-oy Fluorescein	46
Tryptophan	DPH O-initiang	40
Fluorescein	Fluorescein	44
BODIPY	BODIPY	57

$R_0^6 = \frac{\phi_D \kappa^2}{2}$	$\frac{9000\ln 10}{28\pi^5 N_A n^4} \int_0^{\infty} F_D(\lambda) A(\lambda) \lambda^4 d\lambda$			
Tab. 9.1. Examples of Förster critical radii				
Donor	Acceptor	R ₀ (Å)		
Naphthalene	Dansyl	~22		
Anthracene	Perylene	~31		
Pyrene	Perylene	~36		
Phenanthrene	Rhodamine B	~47		
Fluorescein	Tetramethylrhodamine	~55		
Fluorescein-5-isothiocyanate	Eosin maleimide	~60		
Rhodamine 6G	Malachite green	~61		
Iryptophan	Dansyl	~21		
Tryptophan	ANS	~23		
Iryptophan	Anthroyl	~25		
Iryptophan	Pyrene	~28		

Differences between Förster (dipole-dipole interaction) and Dexter (electron exchange) energy transfer processes

- The rate of dipole-induced energy transfer decreases as R⁻⁶ whereas the rate of exchange-induced transfer decreases as *e*-(2r/L). Quantitatively, this means that *k*_{ET} (exchange) drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å)
- The rate of dipole-induced transfer depends on the oscillator strength of the *D → D and A → *A radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the *D → D and A → *A transitions





A Theory of Sensitized Luminescence in Solids, D. L. Dexter, J. Chem. Phys. 21, 836 (1953) Transfer mechanisms of electronic excitation, Th. Forster, Discussions Faraday Soc. 27, 7, (1959)

CHM 535/635 Molecular and Supramolecular Photochemistry

Energy Transfer

Chapter 7 Principles of Molecular Photochemistry: An Introduction NJT, VR and JCS

What is FRET?

- Förster Resonance Energy Transfer
- Radiationless energy transfer between a donor (D) and an acceptor (A) with finite probability based on proximity
- Energy is transferred through the resonant coupling of the dipole moments of D and A

Ideal conditions for FRET

- Donor has a high quantum yield
- There is substantial spectral overlap
- The dipoles of the donor and acceptor can align properly
- The donor and acceptor are at a proper distance

Determination of FRET efficiency

Intensity based:

- Sensitized emission of the acceptor (provided it is fluorescent)
- Decrease in intensity (quenching) of donor fluorescence

Kinetic based:

- Decrease in lifetime (quenching) of donor fluorescence
- Fluorescence decay of acceptor It contains a rise in the initial phase corresponding to the kinetics of donor deexcitation by FRET (a component with "negative amplitude" in the fitted decay)

The use of donor fluorescence is usually preferred, because the acceptor is usually to some extent excitable by the excitation wavelength of the donor – only a part of acceptor fluorescence is a result of FRET











First step	o in experiment	al verifica	tion of Förs	ster formu	lation			
An Experimental Study of the Transfer of Energy of Excitation between Unlike Molecules in Liquid Solutions ¹								
BY EDMUND J. BOWEN AND ROBERT LIVINGSTON								
	J. Am. Chem. Soc., 76, 6300, 1954							
SUMMARY OF THE RATE CONSTANTS AND RELATED QUANTITIES								
B Solvent	Chloroanthracene perylene benzene	Chloroanthracene perglene chloroform	Chloroanthracene perylene liquid paraffin	Chloroanthracene rubrene benzene	Cyanoanthracene rubrene benzene			
R:/1. Å.	41	(42)	(39)	38(?)	84			
An Experimental Study of Energy Transfer between Unlike Molecules in Solution BY WILLIAM R. WARE J. Am. Chem. Soc., 83, 4374, 1961								
	Pair		k₅ (exp.), M ⁻¹ sec. ⁻¹	R ₀ , Å. R (th.) (a, Å. exp.)			
Anthracene*-perylene			1.2×10^{11}	31	54			
Perylene*-rubrene			1.3×10^{11}	38	65			
9,10-Dichloroanthracene*-perylene			8.0×10^{10}	40	67			
Anthracene [*]	-rubrene		3.7×10^{10}	23	39			
9,10-Dichlor	oanthracene*-m	ıbrene	3.1×10^{10}	32	49			
9,10-Dichlor	oanthracene*-r	ibrene	3.1×10^{10}	32	49			





















GFP - Green Fluorescent Protein

- GFP is from the chemiluminescent jellyfish (Aequorea Victoria)
- excitation maxima at 395 and 470 nm (quantum efficiency is 0.8) leads to emission at 509 nm
- contains a *para*-hydroxybenzylideneimidazolone chromophore generated by oxidation of the Ser-Tyr-Gly at positions 65-67 of the primary sequence
- Major application is as a reporter gene for assay of promoter activity
- requires no added substrates

































