

INTERACTION OF PHOTOEXCITED AROMATIC COMPOUNDS WITH TRIFLUOROACETIC ACID

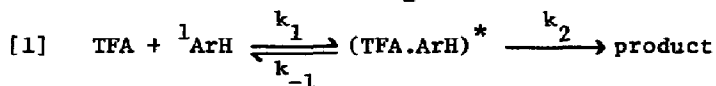
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Trifluoroacetic acid (TFA) enters into a number of photoreactions with aromatic compounds. These include hydrogen exchange in aromatic hydrocarbons¹, acceleration of the dechlorination of a dichlorobiphenyl², reaction with benzene³, and catalysis of the addition of ether to benzene.⁴ The aim of our research is to discover what mechanistic links may exist between these reactions.

Lodder and Havinga² reported that the hydrogen exchange reaction is first order in TFA. They suggested that this may be a rare example of photoelectrophilic substitution. In our studies, we have some evidence (lack of triplet sensitisation) that the reaction derives from the singlet state. In alkane solvents, the usual reaction media, TFA quenches the fluorescence of simple aromatic compounds. The quenching constant exhibits a small deuterium isotope effect. Singlet quenching by TFA thus appears to be intimately related to the hydrogen exchange reaction.

A curious feature of the fluorescence quenching is its solvent dependence: essentially no quenching is observed in polar solvents such as ether or alcohols. For a series of substituted naphthalenes whose lifetimes were known⁵, k_q is essentially independent of the identity of the substituent. This suggests either that proton (H^+) transfer is not involved, or that quenching is reversible. For the quenching scheme of eq. 1, the quenching constant $k_q \tau$ is replaced by $k_1 k_2 (k_{-1} + k_2)^{-1} \tau$; conceivably the factor $k_2 (k_{-1} + k_2)^{-1}$ could change in such a way as to oppose changes in k_1 .



Quenching of the methoxynaphthalenes is considerably more efficient than the other examples, but here proton transfer to oxygen is most probably involved.⁶

Nordblom and Miller² found that TFA accelerated the photodechlorination of 4,4'-dichlorobiphenyl in ether as solvent. Other solvents were without effect. We have confirmed the result for both 4,4'-dichlorobiphenyl and for 1-chloronaphthalene. When deuterated TFA is used, the reaction quantum yield

exhibits an isotope effect, and deuterium is incorporated into both the reduction product and into the "unreacted" aryl halide. This reaction also involves a singlet state. Although no detectable fluorescence quenching is observed, this may be the result of the low absolute value of the reaction quantum yield ($<10^{-2}$).

In the case of the addition of ether to benzene⁴ it was suggested that the reaction involves a combination of electron transfer from ether and proton transfer from TFA. This might parallel the dechlorination in that i) the latter reaction is unsuccessful in hydrocarbons ii) an intermediate would be formed from which Cl[·] could be expelled to give the product iii) there is some resemblance to the well known assistance to photodechlorination of aryl chlorides by amines. However, ether itself does not quench the fluorescence of either of the two chlorides we have studied to any significant extent.

References

1. Lodder and Havinga, *Tetrahedron*, **28**, 5583 (1972).
2. Nordblom and Miller, *J. Agr. Food Chem.*, **22**, 57 (1974).
3. Bryce-Smith, Cox, and Gilbert, *Chem. Comm.*, 914 (1971).
4. Bryce-Smith and Cox, *Chem. Comm.*, 915 (1971).
5. Lentz, Blume and Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, **74**, 484 (1970).
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Table 1: Acid Quenching of the Fluorescence of Aryl Chlorides

Acid	Solvent	k_q (M^{-1})
<u>A: 1-Chloronaphthalene</u>		
TFA	isooctane	1.8
TFA-d	isooctane	0.8
Cl ₃ CCO ₂ H	isooctane	8.4
acetic	isooctane	no quenching
acetic	ether	no quenching
TFA	ether	no quenching
<u>B: 4,4'-Dichlorobiphenyl</u>		
TFA	isooctane	3.2
TFA-d	isooctane	3.0
TFA	ether	no quenching
TFA	methanol	no quenching
HCl	methanol	no quenching

Table 2: Aromatic Fluorescence Quenching by TFA in Isooctane^a

Compound	$k_q \tau (M^{-1})$	$\tau (ns)$	$k_q (1 \text{ mol}^{-1} \text{ s}^{-1})$
PhH	18	33.6	5.3×10^8
PhCH ₃	26	35.2	7.3
PhC ₂ H ₅	14	35.1	3.9
Ph-n-C ₃ H ₇	15	36.0	4.1
Ph-i-C ₃ H ₇	25	36.0	10.2
Ph-n-C ₄ H ₉	21	29.2	7.1
Ph-i-C ₄ H ₉	16	33.3	4.8
Np-H	15.6	96	1.6
α -NpCH ₃	26.8	67	4.0
β -NpCH ₃	22.0	59	3.7
α -NpF	10.6	39	2.7
β -NpF	8.0	18	5.6
α -NpCl	1.8	2.4	7.5
β -NpCl	1.6	4.2	3.9
α -NpOCH ₃	58	25	23
β -NpOCH ₃	64	11	58

a: Ph = C₆H₅, Np = C₁₀H₇