

ORIENTATION AND DISTANCE REQUIREMENTS FOR ENERGY TRANSFER BETWEEN TRIPLET  
ALKYLBENZENES AND BIACETYL AND CIS-PIPERYLENE VAPORS

M. Schuh

Department of Chemistry, Davidson College, Davidson, N.C. 28036 (U.S.A.)

Introduction

Bimolecular electronic energy transfer occurs by at least two mechanisms<sup>1</sup>: (1) electron exchange interaction requiring close contact of donor and acceptor molecules and (2) resonance energy transfer over large distances up to 50 Å, arising from dipole-dipole interactions. Transfer of singlet energy may occur by both mechanisms, whereas spin conservation requirements permit triplet energy transfer only by an electron exchange mechanism.

The requirement of a collision during electron-exchange energy transfer should make steric hindrance likely when bulky groups surround the chromophores of the donor and or acceptor. Yet steric hindrance to energy transfer has been reported in only a few instances<sup>2-6</sup>, none of which involve transfer of triplet energy in the vapor phase. Furthermore, little is known about distance and orientation requirements for efficient energy transfer. In some cases these are best studied in the transfer of triplet state energy in the vapor phase where diffusional contact between donor and acceptor molecules is unrestricted by solvent molecules, and the effects of a solvent cage and static quenching are absent.

This paper reports rate constants for quenching of triplet state alkylbenzenes by cis-piperylene and biacetyl which have been measured in the vapor phase using the flash sensitized biacetyl emission method developed by Parmenter and Ring<sup>7</sup>. Steric hindrance to energy transfer is significant only for 1,4-di-*t*-butylbenzene, and it is concluded that energy transfer is most efficient for a coplanar orientation of alkylbenzene and biacetyl or cis-piperylene at a distance 4.0 to 5.5 Å.

Experimental

All experiments were done at 26°C except the studies of 1,4-di-*t*-butylbenzene which were done at 58.5 ± 0.5°C.

The experimental method has been described previously.<sup>7,8</sup>

The excitation flash ( $\tau_{1/2} = 7 \mu \text{ sec}$ ) is fitted by the sum of two exponentials, and an integrated equation for the concentration of triplet state biacetyl vs time is obtained by solving the rate equations for singlet alkylbenzene, triplet alkylbenzene and triplet biacetyl concentrations. The biacetyl phosphorescence has a time profile which arises from competition between biacetyl formation, which dominates at short times and leads to increasing intensity, and biacetyl triplet decay, which dominates at long times and occurs exponentially with lifetime  $\tau_T$ .  $\tau_T$  and  $t_{\text{max}}$ , the time when phosphorescence reaches its maximum, are the two experimental parameters. These are used with the integrated equation for biacetyl triplet concentration to determine the triplet state lifetime of alkylbenzene,  $\tau_A$ , as a function of biacetyl or cis-piperylene concentration.  $\tau_A$  is expressed as

$$\tau_A^{-1} = k_{GT} + k_{AT}(A) + k_{BT}(B) + k_{cPT}(cP), \quad (1)$$

where A, B, and cP refer to alkylbenzene, biacetyl and cis-piperylene, respectively.  $k_{BT}$  and  $k_{cPT}$  are obtained from the slopes of plots of  $\tau_A^{-1}$  vs (B) and  $\tau_A^{-1}$  vs (cP), respectively.

This method was used for all alkylbenzenes except t-butylbenzene and 1,4-di-t-butylbenzene. For these two molecules the area under the oscilloscope intensity vs time profile, which is proportional to the quantum yield of phosphorescence, was measured. These quantum yields along with estimates of  $\tau_A$ , obtained using the flash sensitization method, were used with the mechanistically appropriate expressions for steady state biacetyl phosphorescence quantum yields to determine  $k_{BT}$  and  $k_{cPT}$ .

### Results

The following table lists values of  $k_{BT}$  and  $k_{cPT}$ .

Alkybenzene	$k_{BT}$		$k_{cPT}$	
	$(10^{10} \text{ M}^{-1}\text{sec}^{-1})$		$(10^{10} \text{ M}^{-1}\text{sec}^{-1})$	
benzene	3.9 ± .5		20 ± 2	
methyl-	6.6 ± .8		18 ± 2	
ethyl-	6.9 ± .8			
n-propyl-	6.8 ± .8		19 ± 2	
t-butyl-	6.7 ± .8		18 ± 2	
1,2-dimethyl-	7.7 ± .9			
1,3-dimethyl-	9.3 ± 1.0			
1,4-dimethyl-	8.8 ± 1.0		16 ± 2	
1,3-diethyl-	10 ± 1		18 ± 2	
1,4-diethyl-	11 ± 1		15 ± 2	
1,4-di-t-butyl-	≤3.1 ± .4		≤7.0 ± .9	
1,2,4-trimethyl-	12 ± 1.5		17 ± 2	
1,3,5-trimethyl-	13 ± 1.5			
1,2,3,4-tetramethyl-	12 ± 1.5			
1,2,3,5-tetramethyl-	15 ± 2		21 ± 2.5	
1,2,4,5-tetramethyl-	14 ± 2		21 ± 2.5	

### Discussion

Our data are supported by the good agreement between the  $k_{cPT}$  value for benzene in the table and that reported in reference 9, which is  $17 \times 10^{12} \text{ M}^{-1}\text{sec}^{-1}$ .

The constancy of  $k_{BT}$  and  $k_{cPT}$  for the mono-alkylbenzenes indicates that the quenching depends little on the lifetime of the collision complex, which is expected to change as the size of the alkyl group changes.

The increase in  $k_{BT}$  with increasing number of substituents on the benzene ring is counter to steric hindrance effects but is consistent with a simple electron exchange mechanism. Moreover, the concomitant decrease in the triplet state energy with increasing substitution leads to an increased overlap between alkylbenzene phosphorescence and  $S_0 \rightarrow T_1$  biacetyl absorption. A similar trend in  $k_{cPT}$  is perhaps not observed because these rate constants nearly equal the hard sphere collisional constant and cannot be much larger.

The table shows that only when two t-butyl groups are present does steric hindrance abruptly reduce  $k_{BT}$  and  $k_{cPT}$ . This apparent similarity in

the optimum separation between alkylbenzene and acceptor is not surprising since both acceptors are similar in size and both possess two double bonds.

Consideration of molecular models reveals that an end-on approach of biacetyl and cis-piperylene perpendicular to the benzene ring should be sterically unhindered in all alkylbenzenes in the table but the decrease in  $k_{BT}$  and  $k_{CPT}$  in the case of 1,4-di-*t*-butylbenzene reveals that this is not the optimum orientation for energy transfer. On the other hand, coplanar approach of donor and acceptor allows maximum overlap of  $\pi$  orbitals and can be sterically hindered. The van der Waals radius for a methyl group is 2.0 Å, and twice this value represents the minimum interplanar distance between polymethylbenzenes and both acceptors at which energy transfer is quite efficient. On the other hand, tertiary-butyl groups extend about 3.5 Å above the benzene plane, and 5.5 Å gives the interplanar distance at which energy transfer abruptly becomes less efficient.

This estimate of 4.0-5.5 Å for optimum energy transfer is the same as that reported by Froehlich and Morrison for quenching of singlet state alkylbenzenes by cis-piperylene in solution<sup>4</sup>, which occurs through vibrational energy dissipation and not electronic energy transfer. However, these workers reported a more gradual decrease in the quenching constant with increasing size of the mono-substituted alkyl group and number of methyl substituents. This may result from the absence of favorable electron exchange interactions, or from a dependence of rate constant on the complex lifetime in a solvent.

Froehlich and Morrison also reported that the quenching constants of a limited number of triplet alkylbenzenes in isopentane at 77°K decrease gradually with increasing size and number of alkyl groups<sup>5</sup>. The difference between solid and vapor phase results may also be due to different collision complex lifetimes in the solid. However the small magnitude of their rate constants (range of 122 to 269 M<sup>-1</sup>sec<sup>-1</sup>) indicates very limited diffusion of donor and acceptor molecules, and the difference in results is more likely due to the random fixed orientations of donor and acceptor molecules in a solid matrix which restricts formation of coplanar states for optimal energy transfer. In this case the efficiency of static energy transfer would be governed principally by the distance between and not orientation of the  $\pi$  orbitals of donor and acceptor molecules. The average distance would increase with increasing substitution and lead to the observed gradual decrease in quenching constant.

#### References

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