DETERMINATION OF TRIPLET QUANTUM YIELDS BY SENSITIZED KETONIZATION OF ETHYL
ACETOACETATE

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A new method for the determination of the quantum yield for intersystem crossing (Q_{TM}) of simple aromatics, especially for benzene and its derivatives, has been developed. It is based on the transfer of the triplet energy of the investigated aromatic donor to ethyl acetoacetate (EAA) as acceptor, which results in a sensitized shifting of the enol – keto equilibrium of EAA (Fig.1). This reaction can easily be followed by spectrophotometry.
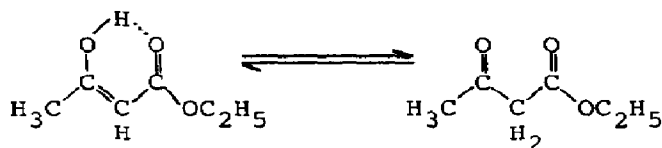

Fig.1: Enol – keto tautomery of ethyl acetoacetate.

The chelated enolic form of EAA shows a strong $\pi\pi^*$-transition at 244 nm and a low lying triplet state (below 370 nm), corresponding to the lowest $n\pi^*$ singlet. In contrast, the diketon of EAA shows above 200 nm only the very weak $n\pi^*$-transition around 275 nm of the carbonyl chromophore /1/.

It has been shown that u.v. irradiation into the characteristic band of the enol with 253.7 nm light causes photoketonization /1,2/. Furthermore, energy transfer from excited molecules of nonpolar and polar solvents, causing also tautomerization, was reported /3/. The formed diketon is the only detectable stable product which reverts slowly to the enol reestablishing the thermal equilibrium.

Because of its low lying triplet state (below 326.5 $kJmol^{-1} \hat{=}$ 78 kcal mol^{-1}), EAA is expected to be an efficient triplet quencher for simple aromatics with the lowest triplet state above this energy. Since carbonyl compounds show generally efficient intersystem crossing, excitation of the donor, followed by triplet-triplet energy transfer, should most propably lead to sensitized ketonization of EAA. This effect could be applied for the determination of the triplet yield of the donor.

In order to test this assumption, various systems i.e. benzene, toluene, p-xylene, anisole and phenol in cyclohexane solution were investigated in this respect. As expected, a decrease of the concentration of the enol following excitation of the donor S_1 state is observed. It was found, that the quantum yield of ketonization at a fixed concentration of the donor increases with the concentration of EAA reaching a plateau values (Q_K^S) above c(EAA) = 1.5×10^{-4} mol dm^{-3}. Thereby no significant quenching of the donor fluorescence by the acceptor was observed in the applied EAA concentration range. This indicates that energy transfer from the donor triplet to the acceptor triplet causes the sensitized ketonization. This energy transfer is diffusion controlled and when the plateau is reached its quantum yield should be unity. In this case Q_K^S is given by:

$$Q_K^S = Q_{TM} \quad Q_K \tag{1}$$

In this formula Q_K stands for the quantum yield for ketonization from the EAA triplet and is taken to be equal to the efficiency for direct photoketonization of EAA, $Q_K = 0.205 \pm 0.01$ (at 24°C).

Applying this method, Q_{TM} values were determined for the above mentioned systems and they are compiled in Table 1.

Compound	Q_{TM}
Benzene	0.235 ± 0.02
Toluene	0.495 ± 0.03
p-Xylene	0.605 ± 0.03
Anisole	0.64 ± 0.06
Phenol	0.32 ± 0.04

Table 1:
Q_{TM} values for various benzene derivatives in dilute cyclohexane solution, determined by sensitized ketonization of ethyl acetoacetate.

As far as data are already determined by other methods our results are in good agreement with these values.

Since singlet processes can be neglected for the EAA concentration normaly used and the product of the isomerization reaction, the diketon, is not further reactive, the performance of the experiments and the evaluation of the results are very simple. When the ketonization is followed by u.v. spectroscopy at 244 nm (also i.r. spectroscopy at 1715 cm^{-1} is applicable) one must pay attention to the absorption properties of the donor and the acceptor in order to allow for optimal conditions in the measurements. Furhtermore the formation of a photoproduct of the donor must be considered. The latter absorbs generally around the characteristic enol band and consequently the results must be corrected for such an effect. Inasmuch as for the irradiation the 254 nm Hg line is used, actinometry can easily be done by following the direct photoketonization of EAA in the same irradiation vessel.

References

/1/ P.Markov and F.Fratev, Compt.Rend.Acad.Buldg.-Sci. 28, 771 (1975)

/2/ P.Markov L.Shishkova and Z.Zdravkova, Tetrahedron Lett. 39, 4017 (1972)

/3/ N.Getoff and F.Fratev, Z.Phys.Chem., N.F., 104, 131 (1977)