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PHOTOREACTIONS OF AROMATIC COMPOUNDS—XXVII*

REINVESTIGATION OF THE PHOTOINDUCED HYDROGEN ISOTOPE EXCHANGE OF SOME AROMATIC COMPOUNDS; PHOTOACYLATION

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Abstract. The photoreactions of anisole, naphthalene, toluene and *p*-xylene in an acidic medium have been studied. Mass spectrometry and radioactivity measurements are applied to study the hydrogen isotope exchange rather than the less adequate 60 MHz NMR technique formerly used. Photochemical hydrogen isotope exchange is established to occur with all four compounds. The reciprocals of the reaction rates (for *p*-xylene and naphthalene) and of the acid concentrations show a linear relationship. The quantum yields measured are considerably lower than those deduced from the earlier work for anisole. Differences can partially be ascribed to several errors.

Besides hydrogen isotope exchange other reactions are found to occur. In the system anisole/acetic acid the main product is 2-hydroxy-acetophenone. Methoxy-acetophenone was also found.

INTRODUCTION

A CONSIDERABLE number of nucleophilic aromatic photosubstitution reactions with various leaving groups and nucleophiles have been discovered and studied.[1-3] As a potential electrophilic substitution reaction photoinduced hydrogen isotope exchange of some substituted benzenes in acidic media was explored in this laboratory some time ago.[4,5] Photodeuteration appeared to occur upon illumination of compounds such as anisole or alkylbenzenes with deuterotrifluoroacetic acid in tetrahydrofuran or n–pentane. However, during continued investigations inconsistent results were obtained and the earlier data appeared to be non-reproducible.†

The originally used 60 MHz NMR technique was considered not sufficiently accurate. A reinvestigation was made applying mass spectrometry for deuterium analysis and radioactivity measurements for experiments with tritiated compounds. By these methods we could establish that photodeuteration and tritiation occur in solutions of anisole or toluene and TFA in n–hexane, albeit with generally lower efficiencies than those deduced from earlier experiments. It was decided to study the reactions in more detail using the better techniques that had become available. Here we

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* Preceding communication; J. A. J. Vink, P. L. Verheydt, J. Cornelisse and E. Havinga, accepted for publication in Tetrahedron.

† At present the picture of photochemical hydrogen isotope exchange in aromatic compounds is rather confusing. Whereas Colpa *et al.*[7] and Kuz'min *et al.*[8] reported hydrogen isotope exchange to occur upon irradiation of some polynuclear hydrocarbons in acidic media and very recently Vesley[9] found effective H-D exchange with quinol in DCl/D_2O, photoexchange was not found by Mason and Smith[10] and Smith[11] with benzene, toluene or naphthalene in 1M perchloric acid nor with anisole or 1,3 dimethoxybenzene in various acidic solvents.

report the photoinduced hydrogen isotope exchange of anisole, naphthalene, *p*-xylene and toluene, the quantum yields, and the orientation patterns of anisole and naphthalene.*

In a following publication fluorescence and quenching experiments will be dealt with and the nature of the reacting excited species will be discussed.*

DISCUSSION

From the experimental data it seems established that alkylbenzenes, naphthalene and anisole undergo hydrogen isotope exchange when illuminated in solutions of trifluoroacetic acid in an alkane.

ϕ increases with increasing concentration of the acidic reagent, $1/\phi$ varies linearly with 1/[acid].

The substitution pattern is different from that found in thermal hydrogen isotope exchange.

The rates of exchange found for anisole in this study appear to be substantially lower than those deduced from our earlier investigations.[4, 5] Some of the deficiencies of the older work became evident in the course of investigations on the photochemical isomerization of some benzenes,[6, 16] where we checked in detail the purification procedures and analytical methods.[6] The analysis of the irradiation products from their 60 Mz NMR spectra yields rather inaccurate results. In some cases—especially when THF had been used as a solvent for the irradiation experiment—the reaction products contained impurities that make the NMR results unreliable. The bromination of anisole in CCl_4 seems to be accompanied by shifting of hydrogens to a considerable degree, leading to erroneous conclusions from the isotope analysis. Furthermore one has to pay attention to the fact that the quantum yield of photodeuteration depends on the D-content of the trifluoroacetic acid. The established sources of error are responsible for part but probably not all of the differences between the earlier results and those reported in this paper.

The much better analytical methods used in this study and the special attention paid to the purification of reaction products make us feel confident that the quantum yields obtained in this investigation can be considered representative. As with other aromatic photosubstitutions there is satisfactory linearity between the reciprocals of the values of the quantum yield and of the concentration of the substituting reagent (TFA). Curiously the substitution patterns are not in line with any of the electron distributions calculated for the S_1, S_2, T_1 and T_2 state.† One might think that for anisole it corresponds to the S_0 distribution (Fig 1). However the differences between the rates of reaction for anisole at the *ortho*, *meta* and *para*positions are relatively small; the rate of *meta* substitution in particular is greater than one should expect from the charge distribution in the ground state. Although it remains possible to qualitatively rationalize this behaviour on the basis of a picture as tentatively

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* An extensive report with full experimental details is to be found in the thesis of one of the authors.[6]

† Calculations were performed by Dr. R. A. van Santen and Mr. W. T. M. Vis of the department of Theoretical Organic Chemistry. The Pariser, Parr and Pople scheme was followed including configuration interaction of all singly excited singlets or triplets respectively.

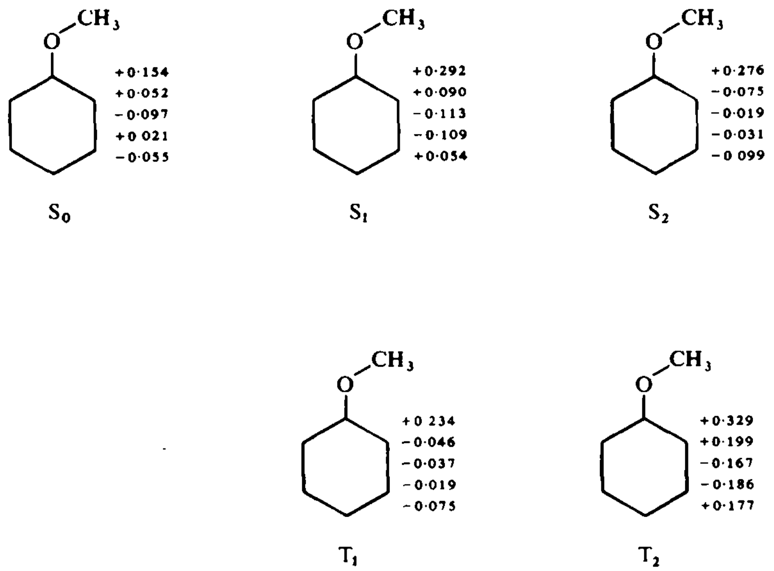

FIG 1. Charge distribution of anisole in the groundstate, the first and second excited singlet and the first and second triplet

developed for the regularities found with nucleophilic photosubstitutions,[14]* the data strengthen our feelings that also emerged from recent results in the latter field:[15] we feel convinced that in the phase now reached progress in understanding these aromatic photosubstitutions will be very difficult unless the reactions are explored in much greater detail by a combination of diversified methods. Some results of orientational research into this direction offered elsewhere,[16,6] also.[15]

PHOTOCHEMICAL ACYLATION

The ultraviolet absorption spectra of mixtures obtained upon irradiation of anisole, alkylbenzenes or naphthalenes and trifluoroacetic acid in n–pentane or n–hexane revealed that other processes take place besides hydrogen exchange. We made a closer investigation of the reaction products of anisole.

The mixture obtained by irradiating this compound with TFA in n–pentane was extracted with water and 2N NaOH. The alkaline solution was neutralized and ether extracted. TLC (silica gel, CH_2Cl_2) showed one major and four minor fractions. Irradiation was then performed on a preparative scale. 12·5 g Anisole in 1·5 l AcOH was irradiated with the light of a S 1200 HP Hg lamp for 26 hrs in a N_2 atmosphere. Chromatography gave 5 fractions. All four minor fractions showed an absorption maximum at 276 nm; their R_f values correspond with those of phenol and 2-, 3- and 4-methylphenol (*Cf.* loc. cit 17).

From the fifth and main fraction 1 g of *o*-hydroxyacetophenone was isolated.

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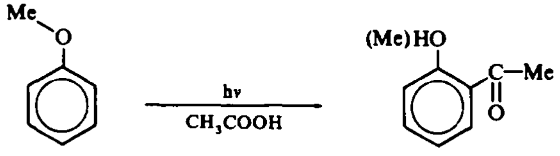
*A possibility one should keep in mind is that the orientation of aromatic compound and acid in an intermediate exciplex, occurring in the reaction determines the course of the substitution.

Since we could demonstrate (mass spectrum) also the presence of methoxyacetophenone in the irradiation mixture we assume that the following reaction occurs:



This reaction, which formally may be described as an (electrophilic) *ortho* photosubstitution, deserves closer mechanistic investigation (cf. also Bryce Smith *et al.*[18, 19]).

EXPERIMENTAL

Photochemical deuterodeprotonation. Toluene (1·9 . 10^{-2} mole/l) and CF_3COOD (90% D, 0·37 mole/l) in n-pentane showed 1·5% exchange (mass spectrometry) after 2 hr illumination with the unfiltered light of a Hanau TQ 81 high pressure mercury lamp. Naphthalene (7·8 . 10^{-3} mole/l, CF_3COOD 0·45 mole/l in n–hexane) and anisole (1·4 . 10^{-2} mole/l, CF_3COOD 0·30 mole/l in n–hexane) contained respectively 0·4% and 0·3% deuterium as a result of similar irradiations.† The use of CF_3COOD with 98% instead of 90% deuterium content resulted in a 2–3 times faster uptake. In the dark with the same systems no exchange could be traced after several hours.

Photochemical tritiodeprotonation. Quantumyields (ϕ) were determined with light of 254 nm wavelength, adopting the photohydrolysis of *meta*-nitroanisole in 0·01 N NaOH containing 2% MeOH as a standard (ϕ = 0·21).[12] Solutions of the aromatic compound (5·79 . 10^{-3} mole/l) and CF_3COOH (T) (0·146 mole/l) in n–hexane were used. The values obtained were: toluene ϕ = 1·3 . 10^{-2}; *p*-xylene: ϕ = 4·4 . 10^{-2}; anisole: ϕ = 6 . 10^{-3}; naphthalene: ϕ = 4 . 10^{-4}. The dark reactions showed only negligible exchange.

Substitution pattern of anisole and naphthalene. Solutions containing 2-d-, 3-d- and 4-d-anisole respectively (2·64 . 10^{-2} mole/l) and CF_3COOH (0·384 mole/l) in n–hexane were irradiated with the light of an S 1200 HP mercury lamp for 6 hr. The solution was kept at 18° in N_2 atmosphere; a reference sample remained in the dark under the same conditions for 312 hr. The results of the deuterium analyses summarized in Table 1, show that the rates of photosubstitution for the *ortho*, *meta* and *para* position in anisole are as 6:1:2. This is different from the pattern obtained in thermal deuterodeprotonation where the relative rate for *meta* substitution is much smaller: *o*:*m*:*p* = 1:0:1.[6, 13]

TABLE 1. PROTODEDEUTERATION OF ANISOLE. D IS PERCENTAGE MONODEUTERO ANISOLE

Anisole	D_1 start	D_1 after irr.	$\Delta D_{irr.}$	D_1 dark*
2-*d*-anisole	87·36	65·35	25·1	86·73
3-*d*-anisole	77·79	75·08	3·5	
4-*d*-anisole	69·24	63·50	8·5	68·97

* After 312 hr.

TABLE 2. PROTODEDEUTERATION OF NAPHTHALENE. D IS PERCENTAGE OF MONODEUTERATED NAPHTHALENE

Naphthalene	D_1 start	D_1 after irr.	$\Delta D_{irr.}$	D_1 dark*
1-*d*-naphthalene	90·81	89·93	0·97	90·88
2-*d*-naphthalene	90·48	90·22	0·29	90·46

* After 168 hr.

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† The experiments with the three compounds were not performed under strictly comparable conditions.

For naphthalene the corresponding data are given in Table 2. The ratio of the rates of the photodeuteration at the α and β position is $\frac{7}{2}$. For the thermal exchange reaction we determined this ratio in separate experiments to be 12/1 (in CF_3COOH).

The substitution patterns of anisole and naphthalene are not blurred by concurrent photochemical isomerization. In independent experiments it was established that upon illumination no (valence) isomerization occurred in naphthalene and (probably) anisole.[6, 16]

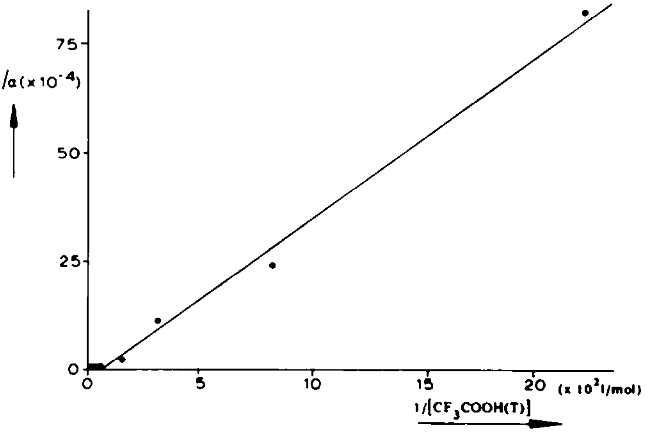

Fig 2. Reciprocal values of the specific activity α of *p*-xylene and the concentration of $CF_3COOH(T)$

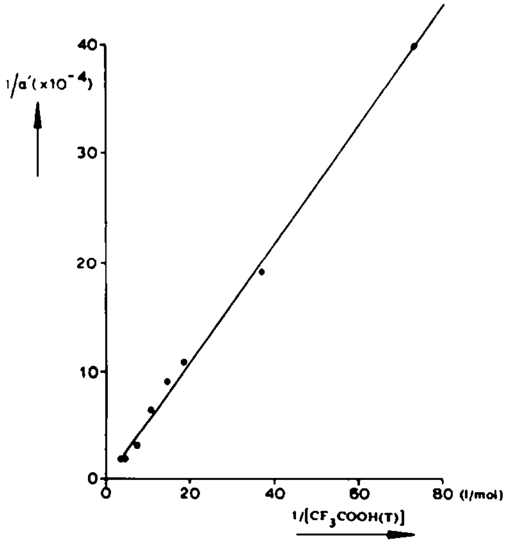

Fig 3. Reciprocal values of the activity (α′) of naphthalene and the concentration of $CF_3COOH(T)$

Influence of $CF_3COOH(T)$ *concentration on the rate of phototritiation of* p-*xylene and naphthalene.* Solutions of *p*-xylene ($1{\cdot}00 \,.\, 10^{-2}$ mole/l) and varying amounts of $CF_3COOH(T)$ in n-pentane were irradiated (TQ 81 HP Hg lamp unfiltered) during 90 min at ~12°. p-Xylene was isolated, its purity checked by GLC and its specific activity measured. Fig. 2 represents the data obtained. Fig. 3 summarizes the results of similar experiments with naphthalene ($1{\cdot}83 \,.\, 10^{-3}$ mole/l) and $CF_3COOH(T)$ in n-hexane as a solvent.

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