Tetrahedron Vol. 35, pp. 63–68

0040–4020/79/0101–0063/$02.00/0

PROPERTIES OF EXCITED SINGLET STATES OF N-ARYLURETHANES

PHOTO-FRIES REACTIONS, FLUORESCENCE, QUENCHING AND SENSITIZATION

K. Schwetlick,* J. Stumpe and R. Noack
Sektion Chemie, Technische Universität Dresden, DDR-8027 Dresden, German Democratic Republic

(*Received in UK* 9 *March* 1978)

Abstract—The deactivation of the first excited S($\pi\pi^*$) states of N-arylurethanes (produced upon irradiation with UV light) by emission (fluorescence), chemical reaction (photo-Fries rearrangement and fragmentation), energy transfer to quenchers, and radiationless transitions to ground and triplet states is investigated. Arylurethanes exhibit fluorescence ($\lambda_f \approx 295-350$ nm, $\phi_f \approx 10^{-2}$, $\tau_f \approx 1-6$ ns) and phosphorescencs ($\lambda_p \approx 370-410$ nm). The variations of the quantum yields of the fluorescence and of the photo-Fries rearrangement of N-arylurethanes by substituents and solvents are essentially due to variations of the rate constants for the radiationless processes. Fluorescence and photo-Fries reactions can be quenched by diffusion-controlled energy transfer to aliphatic ketones. Quenching is accompanied by sensitization of the ketone fluorescence. The urethane fluorescence and photo reactions may be sensitized by aromatic hydrocarbons. The results of all the quenching and sensitization experiments demonstrate that the photo-Fries reactions of N-arylurethanes proceed via the first excited singlet states of the urethanes.

N-Arylurethanes react upon irradiation with UV light mainly to rearrangement and fragmentation products: aminobenzoates and anilines.[1-11]

The mechanism of these photo reactions should be similar to that of the photo-Fries rearrangement of carboxylic esters and amides, which has been investigated in a large number of papers[12] since its first observation by Anderson and Reese in 1960.[13] But up to a few years ago there was no uniform view about this mechanism and only the CIDNP investigations of Adam,[14] the flash photolysis experiments of Kalmus and Hercules,[15] and the gas phase photolysis experiments of Hammond and Meyer[16] and Shizuka[17] have settled the problem to some extent. According to these and other available evidence, the photo-Fries reaction of carboxylic aryl esters and amides involves the cleavage of the O–CO or N–CO σ-bond in the first exited singlet state forming two free radicals, which either recombine in the solvent cage to form the rearranged products or escape out of the solvent cage by diffusion and react to give the fragmentation products by H-abstraction.

Although the photo-Fries reactions of N-arylurethanes have been extensively studied in a phenomenological sense,[1-11] there is only limited information about the nature of the electronically excited states involved. In the present paper we deal with the latter problem by absorption and emission spectroscopy and by kinetic investigations of energy transfer (singlet quenching and sensitization). For the first time, we will report the observation of fluorescence[18] and phosphorescence of N-arylurethanes, their fluorescence lifetimes,[18] as well as the quenching of fluorescence[19] and photo-Fries reactions by ketones.

UV absorption and emission of N-*arylurethanes*

The UV absorption spectra of N-arylurethanes exhibit two characteristic bands in the range of 200–300 nm, showing the typical features of the spectra of substituted benzenes. In the case of N-phenylurethane in cyclohexane maxima are found at 274 nm with an extinction coefficient of 10^3 l. mol^{-1} cm^{-1} and at 233 nm with $\epsilon = 1.7 \times 10^4$ l. mol^{-1} cm^{-1} (Fig. 1). Polar solvents cause a slight red shift of 3–4 nm. Electron-donating substituents in the aromatic ring exhibit the same effect (Table 1). The values of the extinction coefficients and the solvent and substituent effects clearly suggest a $\pi\pi^*$ character of the first excited singlet states involved.

N-Arylurethanes exhibit a rather strong fluorescence with maxima between 295 and 350 nm (Fig. 1), quantum yields in the range of $1-5 \times 10^{-2}$, and lifetimes of 1–4 nanoseconds determined by single photon counting (Table 1). Polar substituents in the aryl group and polar solvents shift the emission to longer wavelengths and the fluorescence quantum yields and lifetimes downwards (Tables 1 and 2). There is a fairly good linear correlation between the lifetimes and the fluorescence quantum yields, showing that the fluorescence rate constants (1)

$$k_f = \phi_f/\tau_f \approx 1.2 \times 10^7 \text{ s}^{-1} \tag{1}$$

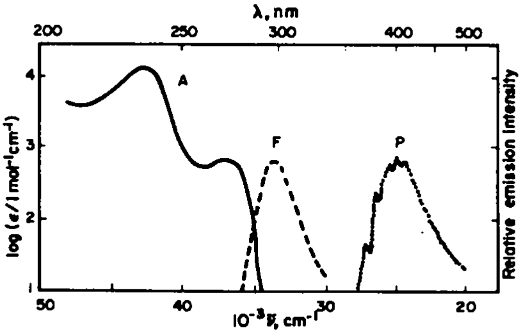


Fig. 1. UV absorption, fluorescence and phosphorescence spectra of N-phenylurethane, (A) absorption in cyclohexane at 20°; (F) fluorescence in heptane at 20°; (P) phosphorescence in 3-methylpentane at 77 K.

Table 1. Spectroscopic properties, energies, fluorescence lifetimes, quantum yields and rate constants of fluorescence and radiationless transitions from the excited singlet state of N-arylurethanes and related compounds in hydrocarbon solvents at 20°

Compound	$\frac{\lambda_a}{nm}$	$\frac{\lambda_f}{nm}$	$\frac{\lambda_p{}^a}{nm}$	$\frac{E_S}{kcal}$	$\frac{E_T}{mol^{-1}}$	$\frac{\tau_f}{ns}$	$\frac{\phi_f}{10^{-2}}$	$\frac{k_f}{10^6 s^{-1}}$	$\frac{k_d + k_{isc}}{10^6 s^{-1}}$
PhNH–COMe	273	314	390	98	80				
PhNH–COPh	265	318	410[b]	99	70[b]				
PhNH–COOEt	273	297	400	100	75	3.8	5.6	15	250
p-MeC$_6$H$_4$NHCOOEt	279	304		103		3.9	6.1	16	240
p-EtOCOC$_6$H$_4$NHCOOEt	261	319		99		1.2	0.3	2	830
p-ClC$_6$H$_4$NHCOOEt	283	311		96		1.0	1.2	12	1000
p-MeOC$_6$H$_4$NHCOOEt	290	318		94		2.5	5.9	24	380
p-Me$_2$NC$_6$H$_4$NHCOOEt	313	354		86		1.6	2.0	12	610
PhNEt–COOEt	275	326	405	96	79	0.8	0.3	4	1200

[a] Phosphorescence measured at 77 K.
[b] In EPA.[20]

Table 2. Lifetimes of the excited singlet state, quantum yields and rate constants of the photo-Fries reaction, fluorescence and radiationless transitions to ground and triplet states of N-phenylurethane at 20°

Solvent	$\frac{\tau_f}{ns}$	$\frac{\phi_f}{10^{-2}}$	$\frac{\phi_r}{10^{-2}}$	$\frac{\phi^2}{10^{-2}}$	$\frac{\phi_3}{10^{-2}}$	$\frac{k_0 + k_p}{10^6 s^{-1}}$	$\frac{k_f}{10^6 s^{-1}}$	$\frac{k_{isc} + k_d}{10^6 s^{-1}}$
n-Hexane	3.8	5.6	2.3	0.86	0.61	3.8	15	240
Diethylether	2.6	4.0	1.3	0.44	0.31	2.9	15	360
Dioxane	2.2	3.1					14	430
Acetonitril	1.8	2.0	1.04	0.34	0.23	3.2	11	540
Ethanol	0.8	0.7	0.46	0.15	0.10	3	9	1200

are essentially the same for all compounds in all solvents studied.

Thus the substituents and polar solvents particularely enhance only the rate constants of radiationsless transitions to ground (k_d) and triplet states (k_{isc}) (2).

$$k_d + k_{isc} \approx (1 - \phi_f)/\tau_f \approx 2, \ldots, 10 \times 10^8\ s^{-1}. \qquad (2)$$

By introducing polar substituents and in polar solvents the Stokes-shifts raise from 3000 to 7000 cm^{-1} indicating increasing differences between the geometries of the excited singlet and ground states.

The energies of the O–O transitions (E_s) calculated from the absorption and fluorescence data are between 95 and 100 kcal mol^{-1} (Table 1), in polar solvents they may be lowered up to 10 kcal mol^{-1}.

The phosphorescence spectra of N-arylurethanes at 77 K in 3-methylpentane show maxima at 370–410 nm (Fig. 1). Singlet–triplet splits of 15–25 kcal mol^{-1} (Table 1) once more indicate a $\pi\pi^*$ character of the excited states involved.

Photo-Fries reactions of N-*arylurethanes*

In the case of N-phenylurethane (1), which we have studied in some detail,[2-6] the main reaction products, upon irradiation with a low-pressure mercury arc under nitrogen, are ethyl o- and p-aminobenzoate (2 and 3), aniline (4), ethane, carbon dioxide (5) and carbon monoxide (6).

Further we have found the by-products urethane (NH$_2$COOEt), formanilide, diphenylurea, N-ethylaniline, ethylene, methane and a polymer consisting of anilino and aminobenzoate units with a molecular weight of 900.

These products can be rationalized by two homolytic scission routes, the main one through cleavage of the N–CO bond (Scheme 2), the other through cleavage of the O–CO bond.[3]

The course of the reaction may be followed by UV-spectroscopy (Fig. 2). The growing band at 280–290 nm is attributed to ethyl p-aminobenzoate, that at 330 nm to the o-aminobenzoate.

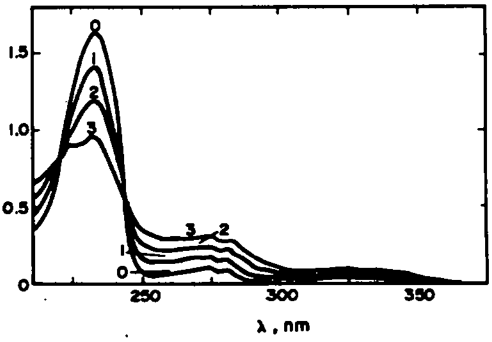
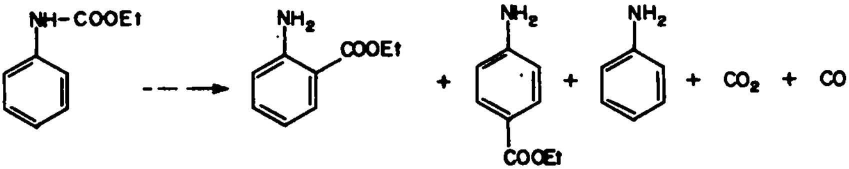


Fig. 2. UV spectra of N-phenylurethane (1) during irradiation at 254 nm in cyclohexane at 20°. [1]$_0$ = 1.0 × 10^{-4} mol l.$^{-1}$.



(3)

1 2 3 4 5 6

The quantum yield of the photo-Fries reaction is independent of the wave length of the exciting UV light. Thus ϕ_2 amounts 7.97 ($\pm$0.05) $\times 10^{-3}$ at 235, 254, 265 as well as 280 nm in cyclohexane at 20°, indicating that the only chemically reactive excited state is the first singlet S_1. S_2 forms S_1 by rapid internal conversion.

The quantum yields for the disappearance of the urethane 1 and for the formation of the photo-Fries products 2 and 3 in several solvents are shown in Table 2. They decrease with increasing ability of the solvents to form H-bonds with the urethane.[6] As the lifetimes of the excited singlet state of 1 fall in the same direction, the rate constants (4)

$$k_0 + k_p = (\phi_2 + \phi_3)/\tau_f \approx 3.2 \times 10^6\ s^{-1} \qquad (4)$$

of the photoreaction calculated according to Scheme 1 are not influenced by the solvent and the observed low quantum yields in polar solvents are completely due to increasing rate constants of the radiationless processes, $k_d + k_{isc}$,

$$1 + h\nu \longrightarrow {}^1 1^*$$
$${}^1 1^* \longrightarrow 1 + h\nu_f$$
$${}^1 1^* \xrightarrow{k_{isc}} {}^3 1^*$$
$${}^1 1^* \xrightarrow{k_d} 1$$
$${}^1 1^* \xrightarrow{k_0} 2$$
$${}^1 1^* \xrightarrow{k_p} 3$$
$${}^1 1^* \xrightarrow{k_s} 4 + \text{polymer} + 5 + 6$$

$$\phi_2 = \alpha k_2 \tau_f$$
$$\phi_2 = k_0 \tau_f$$
$$\phi_3 = k_p \tau_f$$
$$\phi_r = \phi_2 + \phi_3 + \phi_4$$
$$\phi_{isc} + \phi_d = 1 - \phi_f(fi\phi_{dis} = (k_{isc} + k_d)\tau_f$$

Scheme 1.

$$k_d + k_{isc} = (1 - \phi_f - \phi_r)/\tau_f \qquad (5)$$

starting from the first excited singlet state of the urethane 1 (Table 2).

In these calculations the back reaction to the starting compound by recombination of the radical pair formed from the excited urethane is enclosed in k_d, and k_0 and k_p are the overall rate constants of formation of 2 and 3 from ${}^1 1^*$. This formation occurs in several steps via dissociation of ${}^1 1^*$ into a radical pair and recombination of that pair to 2 and 3 and also to the starting compound 1,[3,5] so that the last three reactions in Scheme 1 may be replaced by those formulated in Scheme 2. In a former communication[5] we have estimated that quantum yields ϕ_b of the back reaction, supposing that the recombinations of the radical pair to 1, 2 and 3 are determined by the spin densities in the anilino radical. The calculated rate constants according to Scheme 2 using these values are listed in Table 3.

$${}^1 1^* \xrightarrow{k_{dis}} [Ph\dot{N}H + \dot{C}OOEt]$$
$$[Ph\dot{N}H + \dot{C}OOEt] \xrightarrow{k_b} 1$$
$$[Ph\dot{N}H + \dot{C}OOEt] \xrightarrow{k_2} 2$$
$$[Ph\dot{N}H + \dot{C}OOEt] \xrightarrow{k_4} 4 + \text{polymer} + 5$$

$$\phi_2 = \alpha k_3 \tau_f$$
$$\phi_3 = \alpha k_3 \tau_f$$
$$\phi_{dis} = \phi_b + \phi_2 + \phi_3 + \phi_4 = k_{dis}\tau_f$$
$$\phi_{isc} + \phi_d = 1 - \phi_f - \phi_{isc} + k_d)\tau_f$$
$$\alpha = \frac{k_{dis}}{k_b + k_2 + k_3 + k_4}$$

Scheme 2.

In comparison with other photo-Fries active aromatic compounds, like carboxylic arylesters and carboxylic anilides, N-arylurethanes exhibit a rather high photostability. In connection with this also contrary to carboxylic derivatives, the fluorescence quantum yields of N-arylurethanes are much higher so that their fluorescence can be detected.

Quenching and sensitization experiments

In order to decide whether the photo reaction occurs from the excited singlet or triplet states, quenching and sensitization experiments have been done.

The fluorescence of aryurethanes is quenched by oxygen. If quenching obeys the Stern–Volmer Equation (7)

Table 3. Quantum yields and rate constants of individual reaction steps in the photo-Fries reaction of N-phenylurethane

Solvent	$\frac{\phi_{dis}}{10^{-2}}$	$\frac{\phi_b}{10^{-2}}$	$\frac{k_{dis}}{10^6\ s^{-1}}$	$\frac{k_b}{10^6\ s^{-1}}$	$\frac{\alpha(k_2+k_3)}{10^6\ s^{-1}}$	$\frac{k_{isc}+k_d}{10^6\ s^{-1}}$
n-Hexane	3.0	0.92	7.9	2.4	3.8	240
Diethylether		0.47		1.8	2.9	
Methanol[a]	0.63	0.14	8	1.8	4	1200

[a] $\phi_r = 0.5 \times 10^{-2}$, $\phi_2 = 0.20 \times 10^{-2}$, $\phi_3 = 0.13 \times 10^{-2}$.

Table 4. Quenching of the fluorescence of N-arylurethanes by oxygen in pentane at 20°

	Aerated		Deaerated		$10^{-10} \times k_q$
Compound	ϕ_f	τ_f/ns	ϕ_{f_0}	τ_{f_0}/ns	$l\ mol^{-1}\ s^{-1}$
PhNHCOOEt	0.056	3.8	0.084	5.4	
p-$MeOC_6H_4NHCOOEt$	0.059	2.5	0.071	3.2	

$$ {}^1 1^* + Q \xrightarrow{k_q} 1 + Q^* \qquad (6) $$

$$ \frac{\phi_0}{\phi} = \frac{\tau_0}{\tau} = 1 + \tau_0 k_q[Q] \qquad (7) $$

quenching rate constants k_q can be calculated with $[Q] = [O_2] \approx 2.0 \times 10^{-3}$ mol l.$^{-1}$ in pentane (Table 4). They correspond to the diffusion rate constant of 3×10^{10} l. mol^{-1} s^{-1} calculated by the simple Debye equation.

When the photo-Fries reaction of N-phenylurethane is carried out in aerated and deaerated solutions, no influence of oxygen on the quantum yields can be detected within the limits of experimental accuracy.

Other typical triplet quenchers of suitable energy like 1,3-cyclohexadiene ($E_T = 54$ kcal mol^{-1}), 1,3-pentadiene ($E_T = 57$ kcal mol^{-1}), naphthalene ($E_T = 61$ kcal mol^{-1}) also do not influence the photo-Fries reaction of N-phenylurethane and other carbonic acid derivatives, indicating theat the triplet state of 1 is not involved in the photoreaction.

However, the reactions and the fluorescence of these compounds are quenched by biacetyl, acetone and other aliphatic ketones. Quenching of the photo reaction obeys the Stern–Volmer Equation 7 (Fig. 3). Bimolecular quenching rate constants k_q were calculated from the slopes ($\tau_0 k_q$) and the independently measured lifetime $\tau_0 = 3.8$ ns (Table 5). Their values are close to those predicted for the diffusion rate constant in cyclohexane by the simple Debye equation. This good correspondence of diffusion and quenching constants opens the possibility to determine lifetimes of excited states by the method of energy transfer.

Obviously, the diffusion-controlled quenching of the excited urethanes by aliphatic ketones takes place by an exchange mechanism of singlet energy transfer, because the low extinction coefficients of the $n\pi^*$ absorptions of the ketones rules out a long-range Foerster resonance mechanism.

The efficiency of quenching may be influenced by solvents and substituents changing the S_1 energies of donors and acceptors. Thus the quenching rate constant k_q for Ph–NEt–COOEt by acetone in cyclohexane amounts only 0.3×10^9 l. mol^{-1} s^{-1} vs $6.8 = 10^9$ l. mol^{-1} s^{-1} for Ph–NH–COOEt.

Table 5. Quenching rate constants for the photo-Fries reaction of N-phenylurethane in cyclohexane at 20°

Quencher	$\frac{\lambda_{max}}{nm}$	$\frac{10^{-9} \times k_q}{l\ mol^{-1}\ s^{-1}}$	$\frac{k_q{}^a}{k_D}$
Biacetyl	450	6.5	1.0
Cyclopentanone	300	6.6	1.0
Cyclohexanone	292	7.8	1.1
Cycloheptanone	286	7.5	1.1
Diisopropylketone	289	10.4	1.5
Acetone	279	6.9	1.0
Ethyl acetate	212	No quenching	
Diethyl carbonate	200	No quenching	

[a] Diffusion rate constant in cyclohexane: $k_D = 6.8 \times 10^9$ l. mol^{-1} s^{-1}.

The fluorescence of arylurethanes is quenched by aliphatic ketones and diketones in the same manner as the photoreaction. Quenching also follows the Stern–Volmer Equation (Fig. 4). The resulting quenching rate constants correspond to those obtained in the photoreaction. For biacetyl as quencher $k_q = 7 \times 10^9$ l. mol^{-1} s^{-1} in cyclohexane and 2.8×10^{10} l. mol^{-1} s^{-1} in n-pentane at 20°.

According to eqn (6) quenching of excited N-phenylurethane should be accompanied by the formation of excited singlet states of the ketone quenchers. In fact, N-phenylurethane is able to sensitize the biacetyl fluorescence. The reciprocal sensitized biacetyl fluorescence quantum yield linearly depends on the reciprocal biacetyl concentration.

$$ \frac{\phi_b}{\phi} = 1 + \frac{1}{\tau_0 k_q[Q]} \qquad (8) $$

(ϕ_b: efficiency of biacetyl (Q) fluorescence from ${}^1Q^*$ = quantum yield of unsensitized biacetyl fluorescence).

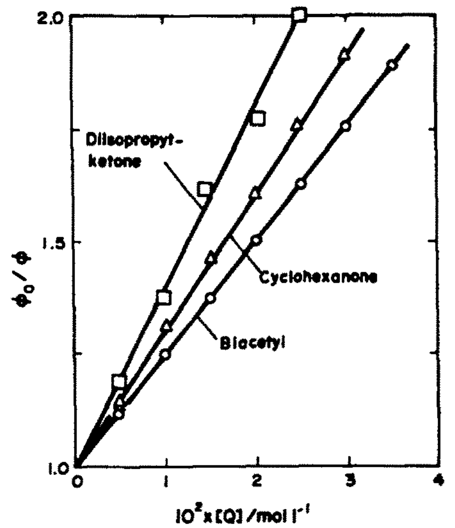


Fig. 3. Quenching of the photo-Fries reaction of N-phenylurethane (5×10^{-3} mol l^{-1}) by aliphatic ketones in cyclohexane at 20°.

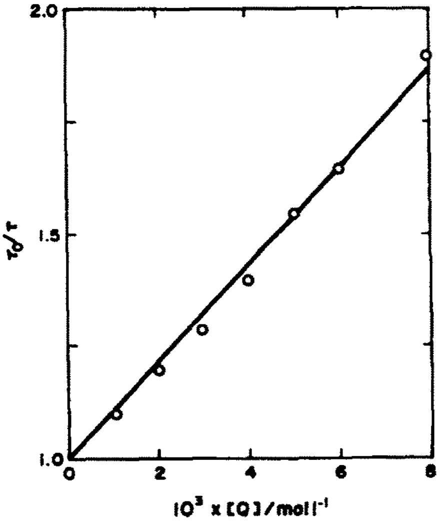


Fig. 4. Quenching of the fluorescence of N-phenylurethane (3×10^{-4} mol l^{-1}) by biacetyl in pentane at 20°.

From the slope a rate constant of $k_q = 8 \times 10^9$ l. mol^{-1} s^{-1} is obtained for the singlet–singlet energy transfer in cyclohexane at 20°, again in good agreement with the quenching rate constants already mentioned.

Thus these identical rate constants determined by independent methods demonstrate that quenching of urethane fluorescence and photoreaction by aliphatic ketones occurs completely by singlet energy transfer.

In accordance with this statement, the photo-Fries reaction of arylurethanes and related compounds may be sensitized by singlet energy transfer from aromatic hydrocarbons (9). Compounds with S_1 levels of higher than 101 kcal mol^{-1} like benzene ($E_s = 106$ kcal mol^{-1}), toluene (106 kcal mol^{-1}) and *p*-xylene (103 kcal mol^{-1}) are suitable as sensitizers. Tetramethylbenzene with a singlet energy of 100 kcal mol^{-1} does not influence the reaction. These results are in good agreement with the O–O-level of excited S_1 state of N-phenylurethane, which has been calculated from spectral data to be $E_s = 100$ kcal mol^{-1} (Table 1).

The kinetics of the arene sensitized photo-Fries reactions are complicated by self quenching of the aromatics (10), in particular of benzene. A kinetic analysis of the measurements is possible.

$$^1S^* + 1 \xrightarrow{k_s} S + {}^1 1^* \tag{9}$$

$$^1S^* + S \xrightarrow{k_{sq}} 2S \tag{10}$$

$$\frac{\phi_a}{\phi} = 1 + \frac{\frac{1}{\tau_s} + k_{sq}[S]}{k_s[1]}. \tag{11}$$

(τ_s: lifetime of $^1S^*$ in the absence of 1. ϕ_a: efficiency of photoproducts formation from $^1 1^*$ = quantum yield of the unsensitized photoreaction).

The reciprocal sensitized photoreaction quantum yields linearely depend on the sensitizer concentration and on the reciprocal urethane concentration. A relevant diagram for benzene as sensitizer is shown in Fig. 5. From the intercept and the slope of the line the energy transfer rate constant k_s and the selfquenching rate constant k_{sq} may be calculated using the excited arene lifetimes of Ivanova *et al.*[21] (Table 6). The energy transfer rate constants for toluene and xylene are in the order of magnitude of the diffusion rate constant (7×10^9 l. mol^{-1} s^{-1}), whereas k_s for benzene is more than 30 times larger than k_D.

Table 6. Energy transfer and selfquenching rate constants in the arene sensitized photo-Fries reaction of N-phenylurethane in cyclohexane at 20°

Sensitizer	$\frac{\tau_{s^a}}{\text{ns}}$	$\frac{10^{-9}\,k_{sq}}{\text{l. mol}^{-1}\,\text{s}^{-1}}$	$\frac{10^{-9}\,k_s}{\text{l. mol}^{-1}\,\text{s}^{-1}}$	$\frac{k_s}{k_D}$
Benzene	5.7	6.5	230	33
Toluene	5.8	2.0	31	4
p-Xylene	6.1	1.6	25	4

[a] In *n*-hexane.[21]

Summarizing the results of all the quenching and sensitization experiments, it could be clearly demonstrated that the photo-Fries reaction of N-phenylurethane proceeds via the first excited singlet state of the urethane. This $S_1(\pi\pi^*)$ state may be populated by direct light absorption or by energy transfer from excited singlet aromatic hydrocarbons (9). It may be deactivated by photo-dissociation (Scheme 2), singlet energy transfer to aliphatic ketones (6), and by radiationless transitions to ground and triplet states (Scheme 1).

EXPERIMENTAL

Materials. The N-arylurethanes have been described in the previous papers. Before use, all compounds were purified by repeated crystallization from petrol-ether or by vacuum distillation. Cyclohexane was purified with HNO_3/H_2SO_4, washed with water, dried with $CaCl_2$ and distilled.

The hydrocarbons were dried and distilled carefully. The ketones were dried with $CaCl_2$ and distilled.

Absorption and emission spectra. Absorption spectra were recorded with a Unicam SP 800 and a Unicam SP 8000 Spectrophotometer. The emission spectra were measured with a Perkin-Elmer Hitachi MPF-2A and Perkin-Elmer-Hitachi MPF-4A. The fluorescence quenching studies were done with a Jobin Yvon Spectrofluorimeter. The relative fluorescence intensities of the urethanes, which were obtained with the MPF-2A and the Jobin Yvon spectrofluorimeters, were corrected against phenol, naphthalene, or *β*-naphthol.[18,19]

For the analysis of the oxygen influence on the fluorescence quantum yields and lifetimes, the samples were degassed on a high vacuum line by several freeze-thaw cycles.

Fluorescence lifetimes. The singlet lifetimes of the aromatic urethanes were measured with a Ortec 9200 Nanosecond Fluorescence Spectrometer by single photon counting after excittation with a air-spark flash or a hydrogen-spark (7 at hydrogen). The light of the hydrogen lamp was filtered by a 5 cm quartz cell containing Cl_2 gas (good transmittance at 265–290 nm and maximum filter effect at the fluorescence maximum wavelength of aromatic urethanes or at wavelengths, at which the lifetime was detected). Glass filters were used for samples which absorbed at 313 nm. The impulse lifetime was 1.3 nsec. In all cases the fluorescence decay was exponential. The fluorescence decay curves were corrected with the decay time of the nanosecond

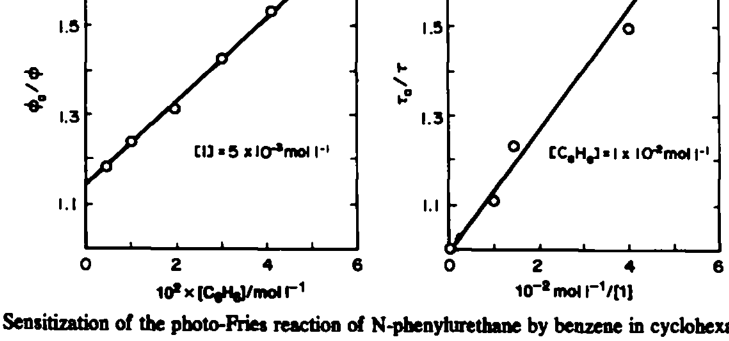


Fig. 5. Sensitization of the photo-Fries reaction of N-phenylurethane by benzene in cyclohexane at 20°.

light pulse, resulting the lifetime of the aromatic urethanes. This correction was necessary, because the lifetimes of the compounds were less than 5 nsec.

$$\tau^2 = \tau^2_{\text{sample}} - \tau^2_{\text{pulse}}.$$

Light sources and actinometry. A low-pressure mercury arc Hanau NN 15/44 VK was used as 254 nm radiation source for the quenching and sensitization experiments of the photoreaction. Acetanilide was used as secondary actinometer.[22] In all cases of quenching, the urethane concentration (10^{-4}–10^{-2} mol/l.) guaranteed that the donator absorbs all the light. In cases, where both donator D and acceptor A absorb, the light absorbed by the donator at 254 nm was evaluated according to

$$\frac{I_D}{I_A + I_D} = \frac{c_D\epsilon_D}{c_D\epsilon_D + c_A\epsilon_A}\left[1 - 10^{-(c_D\epsilon_D + c_A\epsilon_A)d}\right].$$

The *photochemical reaction* was carried out in a 3 ml quartz cell, which also was used for the measurement of the photochemical turnover (formation of the ortho photo-Fries products). The solution was stirred with a magnet in glass, so that the same concentration of the urethane and the photoproducts was maintained in all parts of the cell. The quantum yields for the formation of the ortho photo-Fries products ϕ_2, which are proportional to the quantum yields for the disapppearance of the urenthanes, were determined spectralphotometrically.

The rate constant k_q for the *quenching* of the N-phenylurethane (D) fluorescence by ketones (A) was determined by measuring the steady-state emission intensities of D in the absence and in the presence of A. It was always corrected for trivial absorption by the acceptor at the exciting wavelength and the corresponding absorbance of the acceptor at the wavelength where the emission was monitored. The quenching measurements were carried out in two different manners:

(1) Right angle illumination. The excitation and emission light was corrected for $d = 1/2$ cell length and the urethane concentrations were small, so that the extinction E at the exciting wavelength of 270 nm was 0.3.

(2) Reflex manner. The cell window was in an angle of 30° to the exciting light and the illumination window was the same, from which the fluorescence light was recorded. The urethane concentrations were greater than in method 1, the light was absorbed in a small layer, so that the correction of the exciting light was smaller ($E_D \gg E_A$). The extinction of this solution at a cell length of 0.1 mm was 0.7.

The results of measurements by both methods were identical.

Sensitization experiments. The quantity ϕ_Q/ϕ in the urethane(1)-sensitized biacetyl(Q) fluorescence (eqn 8) was calculated according to

$$\frac{\phi_Q}{\phi} = \frac{\dfrac{I_1}{I_1 + I_Q}}{\dfrac{F}{F_0} - \dfrac{I_Q}{I_Q + I_1}}$$

where F and F_0 are the biacetyl fluorescence intensities with and without 1, and I_1 and I_Q are the light intensities absorbed by 1 and biacetyl, respectively.

ϕ_S/ϕ in the arene(S)-sensitized photo-Fries reaction of 1 (eqn 11) was calculated according to

$$\frac{\phi_S}{\phi} = \frac{\dfrac{I_S}{I_1 + I_S}}{\dfrac{r}{r_0} - \dfrac{I_1}{I_1 + I_S}}$$

where r and r_0 are the reaction rates with and without sensitizer, respectively, and I_S is the light intensity absorbed by the sensitizer.

Acknowledgements—We wish to thank Prof. M. G. Kuzmin from Lomonosov University of Moscow for giving us the possibility to measure the fluorescence lifetimes.[18,19] This work was supported by VEB Synthesewerk Schwarzheide.

REFERENCES

[1] D. Bellus and K. Schaffner, *Helv. Chim. Acta* 51, 221 (1968).

[2] D. J. Trecker, R. S. Foote and C. L. Osborne, *Chem. Commun.* 1034 (1968).

[3] K. Schwetlick, R. Noack and G. Schmieder, *Z. Chem.* 12, 107 (1972).

[4] R. Noack and K. Schwetlick, *Ibid.* 12, 108, 109, 140 (1972).

[5] R. Noack and K. Schwetlick, *Ibid.* 12, 143 (1972).

[6] R. Noack and K. Schwetlick, *Tetrahedron* 30, 3799 (1974).

[7] H. J. Hageman, *Rec. Trav. Chim.* 91, 362 (1972).

[8] H. C. Beachell and L. C. Chang, *J. Polym. Sci.* Part A-1, 10, 503 (1972).

[9] H. Schultze, *Z. Naturforsch.* 28b, 339 (1973).

[10] D. Masilamani, R. O. Hutchins and J. Ohr, *J. Org. Chem.* 41, 3687 (1976).

[11] Y. Takanaka, T. Tomoyuki, T. Ishii and T. Handa, *Nippon Kagaku Kaishi* 462 (1976).

[12] For a review see: D. Bellus, *Adv. Photochem.* 8, 109 (1971).

[13] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.* 217 (1960).

[14] W. Adam, J. A. de Sanabia and H. Fischer, *J. Org. Chem.* 38, 2571 (1973); W. Adam, *Chem. Commun.* 289 (1974).

[15] C. E. Kalmus and D. M. Hercules, *Tetrahedron Letters* 1575 (1972); *J. Am. Chem. Soc.* 96, 449 (1974).

[16] H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan* 42, 909 (1969).

[17] J. W. Meyer and G. S. Hammond, *J. Am. Chem. Soc.* 92, 2187 (1970); 94, 2219 (1972).

[18] See also: J. Stumpe, R. Noack, K. Schwetlick and M. G. Kuzmin, *Vestnik Moskovskogo Universiteta* in press.

[19] See also: J. Stumpe, K. Schwetlick and M. G. Kuzmin, *Ibid.* in press.

[20] E. J. O'Connell, M. Delmauro and J. Irwin, *Photochem. Photobiol.* 14, 189 (1971).

[21] T. V. Ivanova, P. I. Kudryashov and B. Ya. Sveshnikov, *Dokl. Akad Nauk SSSR* 138, 572 (1961).

[22] H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan* 41, 2343 (1968).