341

ENERGY TRANSFER FROM EXCITED CYCLOHEXANE TO AROMATIC SOLUTES

L. WOJNÁROVITS

Institute of Isotopes of the Hungarian Academy of Sciences, P.O. Box 77, H-1525 Budapest (Hungary)

Summary

Energy transfer processes in cyclohexane solutions of ten aromatic compounds were investigated at 25 °C under steady state 7.6 eV photolysis. The transfer rates calculated by taking 1 ns for the excited state lifetime of cyclohexane are equal to or lower than the rates for diffusion-controlled reactions when the reaction radius is taken as the sum of the molecular radii of the solute and solvent molecules. These compounds are found to be good energy quenchers in photolysis experiments and had earlier been reported to be good charge scavengers during radiolysis. It is suggested that some type of short-range interaction is of importance in determining the transfer rates.

1. Introduction

By irradiating liquid cyclohexane at photon energies slightly above the absorption onset (7.0 eV [1]) three primary transformations were identified: molecular hydrogen and hydrogen atom detachments, for which the quantum yields Φ are 0.85 and 0.14 [2, 3], and fluorescence for which $\Phi = 0.01$ [4]. Quenching of the excited state has often been investigated by measuring the fluorescence, in pulsed [5 - 9] and stationary [10, 11] experiments, or the hydrogen yield [2, 12 - 14] in steady state experiments. From the steady state experiments, when the ratio of the quantum yields in the absence and in the presence of a quencher showed a linear dependence on the solute concentration c, the researchers calculated the quenching constant K from $\Phi^0/\Phi = 1 + Kc$. According to the Stern–Volmer theory, K is related to the transfer rate constant k_t: $K = k_t \tau_0$, where τ_0 is the excited state lifetime. The first investigations of the fluorescence decay of cyclohexane indicated that $\tau_0 = 0.3$ ns [15]; more recent measurements have yielded a longer lifetime [16 - 18], some of them suggesting $\tau_0 \geqslant 1$ ns [6, 9, 19].

On the basis of a Stern–Volmer analysis of hydrogen measurements and assuming $\tau_0 = 0.3$ ns, Wada and Hatano [14] established very large transfer rates in cyclohexane solvent. In some cases the rate constant exceeds that calculated with the help of the Stokes–Einstein–Smoluchowski

(SES) equation for diffusion-controlled reactions by one order of magnitude: $k_{SES} = 8RT/3000\eta$, where η is the solvent viscosity and T is the temperature. This contradiction was interpreted in terms of a high reaction radius for the transfer. Large transfer radii are also suggested for some other alkanes [8, 11].

Recently many theoretical and experimental papers have indicated the failure of both SES theory and simple Stern–Volmer theory to describe the quenching processes for short lifetimes [6, 7, 11, 20]. For example, in some experiments at higher solute concentrations ($c \geqslant 0.05$ - 0.15 M) the (Φ^0/Φ)–c curves showed an upward curvature. Transient quenching effects [6, 7, 11] or static quenching effects [20, 21] are suggested to explain this departure from linearity. As was demonstrated by André and coworkers [20, 21] these effects are also important at low concentrations, where the dependence on c is approximately linear as in Stern–Volmer kinetics. They suggested the use of the following simplified equation:

$$\frac{\Phi^0}{\Phi} = 1 + \left\{ NV_1 + k_0\tau_0 + k_0\tau_0 \frac{\sigma'}{(D\tau_0)^{1/2}} \right\} c \tag{1}$$

where $k_0 = 4\pi N\sigma' D$, N is Avogadro's number, σ' is the reaction radius referred to as the "kinetic" distance and D ($= D_S + D_s$) is the sum of the diffusion coefficients of the solute and solvent molecules. V_1 is defined as the volume around an excited molecule, where instantaneous quenching occurs:

$$V_1 = \frac{4}{3}\pi(\sigma'^3 - \sigma^3)$$

where σ ($= r_S + r_s$) is the collisional distance, i.e. the sum of the molecular radii of the solute and solvent molecules. The first term in the braces, NV_1, takes into account the "static" quenching arising from the quencher molecules located between distances σ and σ'. The second term, $k_0\tau_0$, describes the usual diffusional quenching, whereas the third term, $k_0\tau_0\sigma'/(D\tau_0)^{1/2}$, is the so-called transient term.

In the present work, utilizing the equation suggested by André and coworkers and taking the new lifetime, we reinvestigate the question of a high k_t value for the excited state quenching of cyclohexane in stationary experiments by means of measuring the yields of the final products. Most of the compounds used by Wada and Hatano are well-known electron scavengers, e.g. CCl_4. The only exception is benzene which does not react with electrons in radiolytic systems. Our choice of aromatic molecules was influenced by this fact. The reactivities towards electrons can be increased and changed systematically by adding electron-withdrawing groups ($-Cl$, $-Br$, $-CH_2Cl$) to the benzene ring or by polycondensation, thereby allowing a correlation to be sought between the molecular properties and the transfer rates.

2. Experimental details

The spectrograde quality cyclohexane (Fluka) was washed with concentrated sulphuric acid and then distilled and treated with silica gel.

An electrodeless bromine discharge lamp was used for the irradiations [22]. The lamp intensity was 8×10^{15} photons s^{-1}. The hydrogen production rate decreased with the irradiation time in bromobenzene solutions. This decrease was probably caused by some brominated hydrocarbon or polymer deposits on the lamp window. The production rates were established by extrapolating the time dependence curves to zero irradiation time for each concentration.
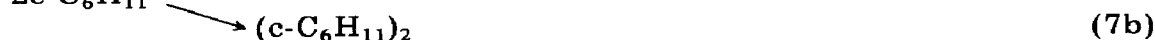
The irradiations were performed by thermostatting the samples at 25 ± 3 °C usually with irradiation times of 4 - 6 min. After photolysis the gas that was not condensable at 77 K was collected and measured in a Toepler pump. The liquid sample was analysed gas chromatographically.

The hydrochloric acid formed in systems containing chlorobenzene and benzyl chloride was measured by titration with an alcoholic solution of $Hg(NO_3)_2$ using diphenylcarbazone as an indicator.

The actinometry was based on the hydrogen yield during the photolysis of pure cyclohexane taking $\Phi(H_2) = 1.0$ as established earlier [14, 22].

3. Results

The decrease in the hydrogen yield in the presence of additives (Figs. 1 and 2) can be related to (1) energy transfer from excited cyclohexane to the solute (this is the main cause in our systems), (2) absorption of radiation at 163 nm by the additive and (3) hydrogen atom scavenging:

$$c\text{-}C_6H_{12} \xrightarrow{\;h\nu\,=\,7.6\ eV\;} c\text{-}C_6H_{12}^* \tag{2}$$

$$S \xrightarrow{\;h\nu\,=\,7.6\ eV\;} S^* \tag{3}$$

$$c\text{-}C_6H_{12}^* \longrightarrow c\text{-}C_6H_{10} + H_2 \tag{4a}$$

$$c\text{-}C_6H_{12}^* \longrightarrow c\text{-}C_6H_{11}^{\,\cdot} + H \tag{4b}$$

$$H + c\text{-}C_6H_{12} \xrightarrow{\;k_a\;} c\text{-}C_6H_{11}^{\,\cdot} + H_2 \tag{5}$$

$$H + S \xrightarrow{\;k_S\;} HS^{\cdot} \tag{6}$$

$$2c\text{-}C_6H_{11}^{\,\cdot} \begin{cases} \longrightarrow c\text{-}C_6H_{12} + c\text{-}C_6H_{10} & (7a) \\ \longrightarrow (c\text{-}C_6H_{11})_2 & (7b) \end{cases}$$

$$c\text{-}C_6H_{12}^* + S \xrightarrow{\;k_t\;} c\text{-}C_6H_{12} + S^* \tag{8}$$

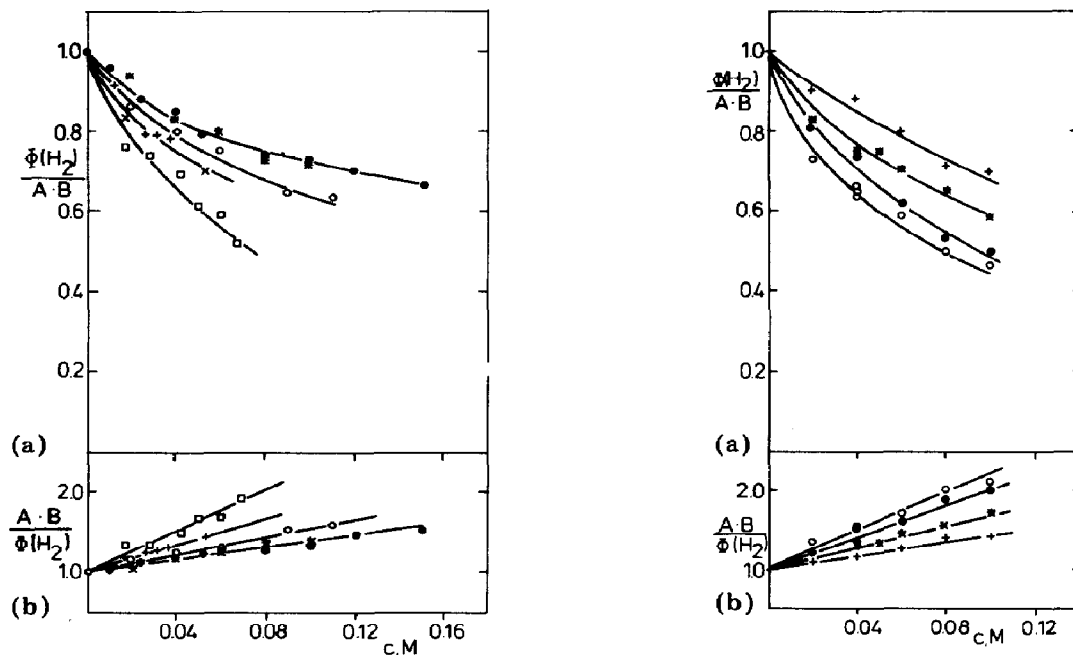(where $c\text{-}C_6H_{12}$ denotes cyclohexane and S denotes the solute).

Fig. 1. (a) Corrected hydrogen yields and (b) quenching plots from cyclohexane—aromatic hydrocarbon systems: ●, benzene; *, toluene; ○, naphthalene; +, phenanthrene; □, *trans*-stilbene.

Fig. 2. (a) Corrected hydrogen yields and (b) quenching plots for cyclohexane solutions with aniline (+), chlorobenzene (*), bromobenzene (○) and benzyl chloride (●).

When the reciprocal of the hydrogen yield is linearly dependent on c with a slope α (and therefore at least formally the Stern—Volmer law is obeyed) the hydrogen formation in solutions is described by

$$\frac{AB}{\Phi(H_2)} = 1 + \alpha[S] \tag{9}$$

A is a factor that corrects for light absorption in the solute:

$$A = \frac{\epsilon_{c\text{-}C_6H_{12}}[c\text{-}C_6H_{12}]}{\epsilon_{c\text{-}C_6H_{12}}[c\text{-}C_6H_{12}] + \epsilon_s[S]} \tag{10}$$

At 163 nm the extinction coefficient $\epsilon_{c\text{-}C_6H_{12}}$ of cyclohexane is equal to 2200 M^{-1} cm^{-1} [23]. The extinction coefficients of the solutes varied between 5000 and 30 000 M^{-1} cm^{-1} [24].

The magnitude of the correction factor B, taking into account the hydrogen atom scavenging, depends on the ratio of the rate constants for the addition (eqn. (6)) and abstraction (eqn. (5)) reactions:

$$B = 1 - \Phi^0(H)\left(\frac{k_S}{k_a}\ \frac{[S]}{[c\text{-}C_6H_{12}]}\right)\bigg/\left(\frac{k_S}{k_a}\ \frac{[S]}{[c\text{-}C_6H_{12}]} + 1\right)$$

$$\approx 1 - 0.14\,\frac{\beta[S]}{\beta[S] + 1} \tag{11}$$

The quantum yield $\Phi^0(H)$ of hydrogen atom elimination in pure cyclohexane was found to be 0.14 [2, 3].

In dilute solution $[c\text{-}C_6H_{12}] \approx [c\text{-}C_6H_{12}]^0$, where $[c\text{-}C_6H_{12}]^0 = 9.3$ M is the molar density of neat cyclohexane. The constant $\beta (= (k_S/k_a)/[c\text{-}C_6H_{12}]^0)$ for some systems (*e.g.* solutions with aromatic hydrocarbons) can be estimated from the dimer yields. For the case when the $HS^{\bullet}$ radicals produced in reaction (6) disappear by reaction with cyclohexyl radicals

$$HS^{\bullet} + c\text{-}C_6H_{11}{}^{\bullet} \longrightarrow \text{products} \tag{12}$$

we developed the following equation:

$$\frac{A\Phi^0((c\text{-}C_6H_{11})_2)}{\Phi((c\text{-}C_6H_{11})_2)} = 1 + (\alpha + \beta)[S] + \alpha\beta[S]^2 \tag{13}$$

By fitting eqn. (13) to the experimental points we obtain two parameters; however, since α and β are interchangeable in eqn. (13), it cannot be stated which of the parameters is equal to α and which to β. As will be seen later the numerical value of one of the parameters is always close to the α value found when the hydrogen yield is analysed. Therefore, this parameter will also be nominated as α.

3.1. Mixtures with aromatic hydrocarbons

It is reasonable to suppose that under our conditions in cyclohexane solvent benzene [12, 14] and other aromatic molecules do not contribute to the hydrogen formation and hydrogen originates entirely from the cyclohexane. The direct light absorption in benzene is low, about 6% at the highest concentration of 0.15 M. We did not find cyclohexadiene, cyclohexyl cyclohexadiene or dicyclohexadienyl among the liquid phase products. This indicates that the cyclohexadienyl radicals produced in reaction (6) do not react with each other, but disappear by disproportionation with cyclohexyl radicals as was suggested by Stone and Dyne [25] from their radiolytic experiments:

$$c\text{-}C_6H_7{}^{\bullet} + c\text{-}C_6H_{11}{}^{\bullet} \longrightarrow C_6H_6 + c\text{-}C_6H_{12} \tag{14}$$
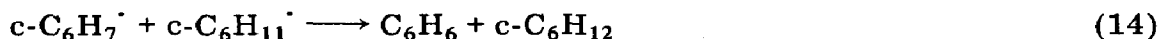
By fitting the dimer yields according to eqn. (13) we obtained 3.7 ± 1.5 M^{-1} and 1.6 ± 0.7 M^{-1} for the two parameters. From the hydrogen yields we calculated $\alpha = 3.8 \pm 0.6$ M^{-1} (Figs. 1 and 3). Our α agrees with the former values 3.5 and 4 M^{-1} found in photolysis at 147 and 163 nm [12, 14]. The value of the constant $k_S/k_a = \beta[c\text{-}C_6H_{12}]^0$ found here to be 15 ± 6 is lower than the value of 35 measured in pulsed experiments [26].

The useful concentration range in mixtures with some of the higher aromatic molecules was strongly reduced by the low solubility. Because of the narrow concentration range ($c \leqslant 0.01$) in anthracene solutions the values for α and β are rough estimates.

In Table 1 the β values and therefore the rates of hydrogen atom addition reactions show a strong dependence on the molecular structure. Comparing our results with those in ref. 27, we found that there is a close
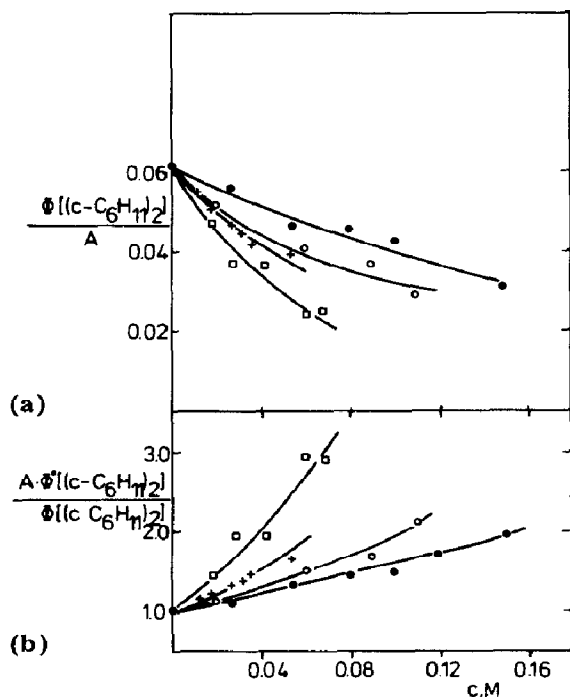
Fig. 3. (a) Corrected dimer yields and (b) quenching plots for some cyclohexane–aromatic hydrocarbon solutions: ●, benzene; ○, naphthalene; +, phenanthrene; □, *trans*-stilbene.

TABLE 1

Aromatic hydrocarbon quenchers

Solutes	α^{a} (M^{-1})	α^{b} (M^{-1})	β (M^{-1})
Benzene	3.8	3.7	1.6
Toluene	4		c
Naphthalene	6.2	7	2
Phenanthrene	9	7	2.5
Anthracene	≈13	—	≈30
trans-stilbene	13	12	7

[a] α was calculated from the hydrogen formation.
[b] α was calculated from the dimer yields.
[c] Not measured; for correction β = 1.5 M^{-1} was applied.

correlation between the rates of methyl radical and hydrogen atom additions: both rates increase with increasing electron affinities of the aromatic hydrocarbons.

3.2. Mixtures with aromatics containing heteroatoms

3.2.1. Cyclohexane–chlorobenzene mixtures

On introducing chlorobenzene into the samples, the quantum yields of hydrogen (Fig. 2) and cyclohexene decrease and that of bicyclohexyl

TABLE 2

Product formation in cyclohexane–chlorobenzene solution

c (M)	$\Phi(H_2)$	$\Phi((c\text{-}C_6H_{11})_2)$	$\Phi(HCl)$	$\Phi(C_6H_6)$	$\Phi_i = \Phi(HCl)/\Delta\Phi(H_2)$
0	1.0	0.062	—	—	—
0.05	0.75	0.13	0.10	0.12	0.40
0.10	0.57	0.09	0.12	0.13	0.28

increases. Benzene and HCl (Table 2) together with very low yields of chlorocyclohexane and phenylcyclohexane can be observed among the liquid phase products. The distribution of products shows that the decomposition of chlorobenzene is sensitized by cyclohexane. The relatively large yield of bicyclohexyl reveals that there are some processes which produce the cyclohexyl radical. The following reactions together with reactions (4), (5), (7) and (8) explain the formation of the main products:

$$C_6H_5Cl^* \longrightarrow C_6H_5Cl \tag{15}$$

$$C_6H_5Cl^* + C_6H_5Cl \longrightarrow (C_6H_5Cl)_2^* \tag{16}$$

$$C_6H_5Cl^* \longrightarrow C_6H_5{}^\cdot + Cl \tag{17}$$

$$Cl + c\text{-}C_6H_{12} \longrightarrow HCl + c\text{-}C_6H_{11}{}^\cdot \tag{18}$$

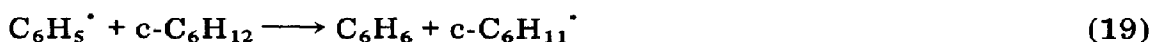$$C_6H_5{}^\cdot + c\text{-}C_6H_{12} \longrightarrow C_6H_6 + c\text{-}C_6H_{11}{}^\cdot \tag{19}$$

Table 2, sixth column, gives the decomposition yield of chlorobenzene relative to the decrease in the hydrogen yield, *i.e.* the intrinsic decomposition yield of $C_6H_5Cl^*$. The decomposition yield decreases with increasing c. A similar dependence on c was observed and attributed to excimer formation by Bunce *et al.* [28] during direct photolysis at 254 nm of chlorobenzene in cyclohexane. It can be supposed that the excited chlorobenzene molecules formed in energy transfer from cyclohexane convert to the same excited state of chlorobenzene (probably S_1) that is also populated when irradiated at 254 nm. This supposition is in agreement with the results of Friedman *et al.* [29] who found that the excited states produced by absorption of light of wavelength 193 nm entirely convert to the S_1 state of chlorobenzene. The energy of light of wavelength 193 nm (6.48 eV) is approximately equal to the energy transferred from cyclohexane to chlorobenzene (the energy of the S_1 state of cyclohexane) in our experiments.

3.2.2. Cyclohexane–bromobenzene solutions

In solutions containing bromobenzene the decrease in the hydrogen yield is also accompanied by the formation of benzene; however, in these mixtures the cyclohexene and bicyclohexyl yields are very low. The quantum yields at a bromobenzene concentration of 0.04 M are as follows: $\Phi(H_2)$,
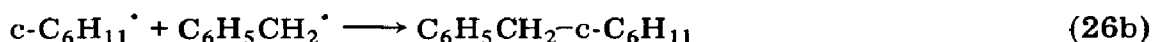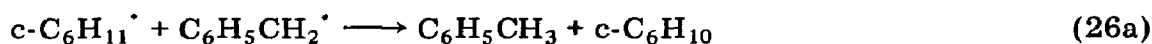
0.66; $\Phi(\text{c-C}_6\text{H}_{10})$, 0.2; $\Phi((\text{c-C}_6\text{H}_{11})_2)$, 0.02; $\Phi(\text{C}_6\text{H}_6)$, 0.2. This behaviour can be understood by the fact that bromine atoms do not abstract hydrogen atoms from cyclohexane molecules because the abstraction is endothermic ($\Delta H^{\circ}_{298\,\text{K, gas phase}} = 33 \text{ kJ mol}^{-1}$). Instead they disappear by other reactions:

$$\text{C}_6\text{H}_5\text{Br}^* \longrightarrow \text{C}_6\text{H}_5^{\cdot} + \text{Br} \tag{20}$$

$$\text{Br} + \text{C}_6\text{H}_5\text{Br} \longrightarrow \text{C}_6\text{H}_5\text{Br}_2^{\cdot} \tag{21}$$

$$\text{Br} + \text{c-C}_6\text{H}_{10} \longrightarrow \text{c-C}_6\text{H}_{10}\text{Br}^{\cdot} \tag{22}$$

$$\text{Br} + \text{Br} \longrightarrow \text{Br}_2 \tag{23}$$

$$\text{c-C}_6\text{H}_{10} + \text{Br}_2 \longrightarrow \text{c-C}_6\text{H}_{10}\text{Br}_2 \tag{24}$$

The low yield of bicyclohexyl and the high yield of benzene indicate that the majority of cyclohexyl radicals formed in the decomposition of cyclohexane or in the hydrogen abstraction by phenyl radicals, instead of undergoing the disproportionation and recombination reactions (7a) and (7b), react with other radicals present, e.g. $\text{C}_6\text{H}_5\text{Br}_2^{\cdot}$, $\text{C}_6\text{H}_5^{\cdot}$ and $\text{Br}^{\cdot}$.

3.2.3. Cyclohexane–benzyl chloride solutions

In mixtures containing benzyl chloride the decrease in the hydrogen yield is accompanied with an increase in bicyclohexyl formation and with the production of toluene, phenylcyclohexane, dibenzyl and HCl reflecting the sensitized decomposition of the benzyl chloride additive. At $c = 0.1$ M the yields are as follows: $\Phi(\text{H}_2)$, 0.5; $\Phi(\text{c-C}_6\text{H}_{10})$, 0.5; $\Phi((\text{c-C}_6\text{H}_{11})_2)$, 0.07; $\Phi(\text{C}_6\text{H}_5\text{CH}_3)$, about 0.03; $\Phi(\text{C}_6\text{H}_5\text{CH}_2\text{-c-C}_6\text{H}_{11})$, 0.08; $\Phi((\text{C}_6\text{H}_5\text{CH}_2)_2)$, 0.05; $\Phi(\text{HCl})$, 0.5. The relevant reactions are the following:

$$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^* \longrightarrow \text{C}_6\text{H}_5\text{CH}_2^{\cdot} + \text{Cl} \tag{25}$$

$$\text{c-C}_6\text{H}_{11}^{\cdot} + \text{C}_6\text{H}_5\text{CH}_2^{\cdot} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{c-C}_6\text{H}_{10} \tag{26a}$$

$$\text{c-C}_6\text{H}_{11}^{\cdot} + \text{C}_6\text{H}_5\text{CH}_2^{\cdot} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{-c-C}_6\text{H}_{11} \tag{26b}$$

$$2\text{C}_6\text{H}_5\text{CH}_2^{\cdot} \longrightarrow (\text{C}_6\text{H}_5\text{CH}_2)_2 \tag{27}$$

Chlorine atoms also produce HCl here as in reaction (18).

3.2.4. Cyclohexane–aniline solutions

The influence of aniline on the hydrogen yield is low, similarly to that of benzene or toluene. When we analysed the solution after irradiation we did not find possible decomposition products such as phenylcyclohexane or biphenyl.

4. Discussion

4.1. Kinetics of quenching: quenching constants

In Figs. 1 and 2 the $AB/\Phi(\text{H}_2)$ values plotted against c show a linear dependence on c. In our experiments a concave upward deviation was not

TABLE 3

Test for diffusion control (parameters connected with eqn. (1))

Solutes	t (°C)	α (M^{-1})	D (×10^{-9} m^2 s^{-1})	σ (nm)	σ' (nm)	p	k_t (×10^{10} M^{-1} s^{-1})
Benzene	25	4	3.2	0.68	0.15	0.2	0.4
Toluene	25	4	2.85	0.71	0.16	0.2	0.4
Naphthalene	25	6.5	2.8	0.71	0.26	0.3	0.65
Phenanthrene	25	9	2.6	0.75	0.37	0.4	0.9
Anthracene	25	13	2.6	0.75	0.5	0.6	1.3
trans-stilbene	25	13	2.6	0.75	0.5	0.6	1.3
Chlorobenzene	25	8	2.85	0.7	0.31	0.4	0.8
Bromobenzene	25	13	2.85	0.7	0.37	0.6	1.3
Benzyl chloride	25	10	2.75	0.71	0.39	0.5	1.0
Aniline	25	3.5	2.8	0.69	0.14	0.15	0.35
CCl$_4$ [a]	25	25	2.93	0.69	0.77	1.0	2.5
SF$_6$ [b]	15	16	2.50	0.6	0.57	0.8	1.5
CO$_2$ [b]	15	15	2.9	0.63	0.49	0.8	1.4
CH$_3$Br [b]	15	16	2.7	0.66	0.54	0.8	1.5
C$_2$H$_5$Br [b]	15	22	2.5	0.69	0.72	1.0	2.0

[a] From ref. 30.

[b] From ref. 14.

observed which disagrees with some fluorescence experiments [6, 7, 11]. The lack of an upward bend may be due to the low quencher concentrations applied and upward curvature can be observed only at higher values of c. Our quenching constants, which are denoted α to show the difference from the Stern—Volmer constant K, are collected in Table 3 together with the α values of Wada and Hatano [14] measured at 15 °C.

In contrast with the hydrogen yield, for the dimer formation when $A\Phi^0((\text{c-}C_6H_{11})_2)/\Phi((\text{c-}C_6H_{11})_2)$ is plotted as a function of c upward curvature does occur. According to our model, however, this is due to hydrogen atom scavenging. The quenching constant established in the hydrogen atom formation appears to be the same as that for the total hydrogen yield. This involves a common excited state that is quenchable by additives for hydrogen and hydrogen atom elimination that was tacitly assumed in the development of eqns. (9) and (13). It was suggested that hydrogen atom detachment takes place from a dissociative triplet state populated by $S_1 \rightsquigarrow T_n$ intersystem crossing [31, 32].

4.2. Energy transfer rates: diffusion-controlled kinetics

As the reciprocal hydrogen yields show a linear dependence on c in our experiments eqn. (1) can be used for the calculation of transfer rates by taking $\alpha = NV_1 + k_0\tau_0 + k_0\tau_0\sigma'/(D\tau_0)^{1/2}$. For the excited state lifetime of cyclohexane at 25 °C we use 1.0 ns which is the average of recent determinations [6, 9, 16 - 19]. Since τ_0 was found to increase with decreasing tempera-

ture for many alkanes [31, 32] we take $\tau_0 = 1.1$ ns at 15 °C. The self-diffusion coefficient of cyclohexane at 25 °C is 1.44×10^{-9} m^2 s^{-1} [33]; for 15 °C we estimated this to be 1.2×10^{-9} m^2 s^{-1}. D_s was taken to be equal to the self-diffusion coefficient of cyclohexane. For some of the quenchers (benzene, aniline, CCl$_4$ [34 - 36]) the previously reported diffusion coefficient D_S in cyclohexane solvent was used; for the other quenchers this parameter was estimated from empirical and semiempirical relations [11, 37, 38] and an average of the different estimates was applied to the calculations. The molecular radius r_s of cyclohexane was taken as 0.35 nm [37] and the r_S values of the solutes were obtained from the literature [37] or calculated from molar volumes. The σ' "kinetic" radius was estimated from quenching data.

Of the quenchers collected in Table 3 we calculated that σ' is greater than σ only for CCl$_4$ and C$_2$H$_5$Br. With these two halogenated compounds some static quenching is also effective. Of course, physically σ' cannot be smaller than the sum of the molecular radii σ. The relation $\sigma' < \sigma$ may reflect that not every encounter of the reactants leads to a transfer. The reaction probability p per encounter can be calculated from the ratio of the observed transfer rate constant k_t (where $k_t = \alpha/\tau_0$ when $\sigma' < \sigma$ and $k_t = k_0\{1 + \sigma'/(D\tau_0)^{1/2}\}$ when $\sigma' > \sigma$) to the diffusion-controlled rate constant k_d (where $k_d = k_0\{1 + \sigma'/(D\tau_0)^{1/2}\}$ when $\sigma' > \sigma$ and $k_d = k_0\{1 + \sigma/(D\tau_0)^{1/2}\}$, taking $k_0 = 4\pi N\sigma D$ when $\sigma' < \sigma$). When $\sigma' < \sigma$ we took $NV_1 = 0$.

It is obvious from Table 3 that our quenching data, and also the recalculated data of Wada and Hatano [14], do not reveal high quenching radii, in contrast with the results of some fluorescence quenching experiments [8, 11]. The reason for this disagreement is unclear as yet. One possibility could be that fluorescence and chemical decomposition occur from two distinct excited states, the quenching rate constants of which are different. However, other experimental data seem to contradict this supposition [39, 40].

Next we examine which factors may influence the magnitude of p and k_t.

According to the Förster theory [41] the rates of singlet–singlet energy transfer are determined by the dipole–dipole interaction which depends on the overlap of donor fluorescence and acceptor absorption spectra. From the relevant data, however, it appears that this factor cannot be of major importance in determining k_t for the quenchers listed in Table 3. For example, there is almost no overlap between the cyclohexane fluorescence spectrum and the absorption spectra of SF$_6$ and CO$_2$, but the values of k_t are high. The overlap of the two spectra is also poor with CH$_3$Br and C$_2$H$_5$Br. For CCl$_4$ the overlap is somewhat higher, and from the Förster equation

$$R_0{}^6 = \frac{9000 \ln 10}{128\pi^5 n^4 N} \frac{2}{3} \int_0^\infty F_s(\tilde{\nu}) \epsilon_S(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \tag{28}$$

we calculated a "critical distance" R_0 of 0.68 nm, which agrees with the contact distance but is much smaller than that found in quenching of excited

states of aromatic molecules (2 - 5 nm) to which the theory has been successfully applied. R_0 is defined as the distance between the solute and the excited solvent molecules for which the rates of deactivation and dipole—dipole energy transfer are equal. It is calculated from eqn. (28), where n is the solvent refractive index, N is Avogadro's number, $F_s(\tilde{\nu})$ is the fluorescence spectrum of cyclohexane normalized to the fluorescence quantum yield and $\epsilon_S(\tilde{\nu})$ is the molar decadic extinction coefficient of the solute. For aromatic quenchers we calculated R_0 values between 1.1 and 1.4 nm but there is no correlation between R_0 and k_t or σ', i.e. R_0 decreases in the order naphthalene > phenanthrene > anthracene whereas k_t increases. It appears that the rates are not determined by the extent of the dipole—dipole interactions.

Several papers [9, 42, 43] suggest a correlation between the transfer rates and the free-energy change of the reaction. The free-energy change is calculated from the energy difference between the donor and the acceptor excited states. Again it seems that this connection is not valid for our systems. For example, the transfer for all aromatic quenchers is highly exothermic and therefore we would expect a similarly large value of k_t for the aromatic quenchers. In contrast, for the non-aromatic molecules this theory predicts a lower k_t value, in disagreement with the experiments.

It was mentioned in Section 1 that the reaction rates between the solutes and the electron vary with the nature of the solute. The electron-donating $-CH_3$ and $-NH_2$ groups on the benzene ring tend to lower the electron affinity and to hinder the formation of aromatic negative ions. Therefore toluene and aniline have less affinity towards electrons than benzene has. It should be noted that for these aromatic molecules we found low rates of transfer. Compared with $-CH_3$ and $-NH_2$, the electron-withdrawing $-Cl$, $-Br$ and $-CH_2Cl$ groups on the benzene ring enhance the reactivity towards electrons and the ability to form negative ions [44]. With these substituents k_t increases by a factor of 2 - 3. The increase in conjugation in the molecule has a similar effect to that of the electron-withdrawing substituents. The gas phase thermal electron attachment rates and electron affinities (which are positive for the polycondensed aromatic molecules [44, 45]) increase in the order naphthalene < phenanthrene < *trans*-stilbene < anthracene, and k_t also tends to increase in the same order.

This finding may suggest that some type of short-range interaction is of importance in the transfer but its nature is unknown as yet. A possibility is that reaction (8) has a two-step mechanism:

$$c\text{-}C_6H_{12}{}^* + S \longrightarrow c\text{-}C_6H_{12}{}^+ + S^- \qquad (29)$$

$$c\text{-}C_6H_{12}{}^+ + S^- \longrightarrow \text{neutral products} \qquad (30)$$

where the temporary charge separation can be exothermic, since in liquid alkanes the polarization around charged species (for which the energy is 1 - 1.5 eV for an elementary charge [46]) strongly decreases the energy demand of the process. With aromatic hydrocarbon quenchers reactions (29)

and (30) lead to a dissipation of the excitation energy of cyclohexane in the vibrational levels. The chlorine-, bromine- and CH_2Cl-substituted benzene anions can easily undergo dissociation by loss of Cl^- or Br^- [47, 48], *e.g.*

$$C_6H_5CH_2Cl^- \longrightarrow C_6H_5CH_2^{\cdot} + Cl^- \tag{31}$$

$$Cl^- + c\text{-}C_6H_{12} \longrightarrow HCl^- + c\text{-}C_6H_{11}^{\cdot} \tag{32}$$

$$HCl^- + c\text{-}C_6H_{12}^+ \longrightarrow HCl + c\text{-}C_6H_{12} \tag{33}$$

In these reactions we expect the formation of chemical decomposition products that are similar to those formed in the neutral energy transfer (eqn. (8)). The product formation in mixtures with chlorobenzene, however, indicates neutral transfer.

Further work is needed to clarify the precise mechanism of transfer and also to find the properties that determine its magnitude.

References

1 W. Rothman, F. Hirayama and S. Lipsky, *J. Chem. Phys., 58* (1973) 1300.
2 L. Wojnárovits and G. Földiák, *Acta Chim. Acad. Sci. Hung., 105* (1980) 27.
3 L. Wojnárovits and G. Földiák, *Zentralinst. Isot. Strahlenforsch. Mitt., Leipzig, 43a* (1981) 243.
4 H. T. Choi, D. Askew and S. Lipsky, *Radiat. Phys. Chem., 19* (1982) 373.
5 W. P. Helman, *Chem. Phys. Lett., 17* (1972) 306.
6 F. Barigelletti, S. Dellonte, G. Mancini and G. Orlandi, *Chem. Phys. Lett., 65* (1979) 176.
7 G. Orlandi, S. Dellonte, L. Flamigni and F. Barigelletti, *J. Chem. Soc., Faraday Trans. I, 78* (1982) 1465.
8 L. H. Luthjens, H. D. K. Codee, H. C. De Leng and A. Hummel, *Chem. Phys. Lett., 79* (1981) 444.
9 R. Hermann, O. Brede and R. Mehnert, in J. Dobó, P. Hedvig and R. Schiller (eds.), *Proc. 5th Tihany Symp. on Radiation Chemistry*, Akadémiai Kiadó, Budapest, 1983, p. 503.
10 L. Walter, F. Hirayama and S. Lipsky, *Int. J. Radiat. Phys. Chem., 8* (1976) 237.
11 H. T. Choi and S. Lipsky, *J. Phys. Chem., 85* (1981) 4089.
12 J. Y. Yang, F. M. Servedio and R. A. Holroyd, *J. Chem. Phys., 48* (1968) 1331.
13 R. A. Holroyd, *Adv. Chem. Ser., 82* (1969) 488.
14 T. Wada and Y. Hatano, *J. Phys. Chem., 81* (1977) 1057.
15 M. S. Henry and W. P. Helman, *J. Chem. Phys., 56* (1972) 5734.
16 W. R. Ware and R. L. Lyke, *Chem. Phys. Lett., 24* (1974) 195.
17 L. H. Luthjens, M. P. De Haas, H. C. De Leng and A. Hummel, *Radiat. Phys. Chem., 19* (1982) 121.
18 H. D. K. Codee, *Thesis*, Rijksuniversiteit Leiden, 1979.
19 Y. Katsumura, Y. Tabata and S. Tagawa, *Radiat. Phys. Chem., 19* (1982) 267.
20 J. C. André, M. Niclause and W. R. Ware, *Chem. Phys., 28* (1978) 371.
21 J. C. André, I. Kawenoki, J. Kossanyi and P. Valat, *J. Photochem., 19* (1982) 139.
22 L. Wojnárovits, L. Kozári, Cs. Keszei and G. Földiák, *J. Photochem., 19* (1982) 79.
23 B. L. Sowers, M. W. Williams, R. N. Hamm and E. T. Arakawa, *J. Chem. Phys., 57* (1972) 167.
24 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol. II, Academic Press, New York, 1974, pp. 209 - 268.
25 J. A. Stone and P. J. Dyne, *Radiat. Res., 3* (1962) 353.

26 M. C. Sauer, Jr., and I. Mani, *J. Phys. Chem.*, *72* (1968) 3856.

27 R. S. Becker and E. Chen, *J. Chem. Phys.*, *45* (1966) 2403.

28 N. J. Bunce, J. P. Bergsma, M. D. Bergsma, W. De Graaf, Y. Kumar and L. Ravanal, *J. Org. Chem.*, *45* (1980) 3708.

29 A. Friedman, S. C. Yang, M. Kowasaki and R. Berohn, *J. Chem. Phys.*, *72* (1980) 1028.

30 R. Hermann, R. Mehnert and L. Wojnárovits, *Ber. Bunsenges. Phys. Chem.*, to be published.

31 L. Flamigni, F. Barigelletti, S. Dellonte and G. Orlandi, *Chem. Phys. Lett.*, *89* (1982) 13.

32 S. Dellonte, L. Flamigni, F. Barigelletti, L. Wojnárovits and G. Orlandi, *J. Phys. Chem.*, to be published.

33 R. Freer and J. Sherwood, *J. Phys. Chem.*, *85* (1981) 102.

34 G. M. Panchenkov, V. V. Erchenkov and N. N. Borisenko, *Sovrem. Probl. Fiz. Khim.*, *14* (1970) 316.

35 J. E. Anderson and W. H. Gerritz, *J. Chem. Phys.*, *53* (1970) 2584.

36 S. H. Chen, H. T. Davis and D. F. Evans, *J. Chem. Phys.*, *75* (1981) 1422.

37 A. H. Alwattar, M. D. Lumb and J. B. Birks, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Vol. I, Wiley, New York, 1973, p. 403.

38 H. Ertl, R. K. Chai and F. A. L. Dullien, *AIChE J.*, *20* (1974) 1.

39 L. Wojnárovits and G. Földiák, *Abstracts 8th IUPAC Symp. on Photochemistry, Seefeld, Tyrol, July 13 - 19, 1980*, p. 372.

40 F. P. Schwarz, D. Smith, S. G. Lias and P. Ausloos, *J. Chem. Phys.*, *75* (1981) 3800.

41 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970, p. 569.

42 F. Busi and G. Casalbore, *Gazz. Chim. Ital.*, *111* (1981) 443.

43 V. Balzani, F. Bolletta and F. Scandola, *J. Am. Chem. Soc.*, *102* (1980) 2152.

44 R. P. Blaunstein and L. G. Christophorou, *Radiat. Res. Rev.*, *3* (1971) 69.

45 L. Wojnárovits and G. Földiák, *J. Chromatogr.*, *206* (1981) 511.

46 S. Lipsky, *J. Chem. Educ.*, *58* (1981) 93.

47 A. Horowitz and L. A. Rajbenbach, *Int. J. Radiat. Phys. Chem.*, *5* (1973) 163.

48 M. Tanaka and K. Fueki, *J. Phys. Chem.*, *77* (1973) 2524.