

## STUDIES ON THE PROCESS OF SENSITIZATION IN THE BENZENE-KETONES SYSTEM BY FLUORESCENCE QUENCHING

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### Summary

Studies were made on the quenching of fluorescence of benzene state  $S_1$ , excited with  $\lambda = 254$  nm radiation, by acetone, 2-butanone and 3-pentanone in cyclohexane, n-heptane, acetonitrile and ethyl acetate. The calculated values of quenching rate constants  $k_q$  suggest that this process is in most cases controlled by diffusion. To furnish an example, the results are presented of investigations on the sensitizing effect of benzene upon the photolysis of acetone in cyclohexane and attempts were made at an analysis of the kinetics of the process.

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### Introduction

The sensitized reactions are the problems most extensively investigated in photochemistry nowadays. The sensitization of photochemical processes of different compounds by means of aromatic compounds [1 - 11] and especially benzene [1 - 3], plays a large role in this field. One of the reasons for which aromatic compounds are widely used as sensitizers is their considerable photochemical passivity at relatively efficient electronic excitation [1, 13]. In the gaseous and liquid phases, by selecting the adequate wavelength of the exciting light, by oxygenation and deoxygenation of the system and application of the right temperature, large and stable molecule concentrations in the  $S_1$  and  $T_1$  states can be obtained.

There are known cases in which benzene, both in the  $S_1$  and  $T_1$  states, sensitizes the photolysis of 4-pentanol, cyclobutanone [10] and some olefins [12].

The transfer of energy of the electronic excitation of the sensitizer to the molecules of the acceptor is the essential process of sensitization. If it occurs by collisions, the process is controlled by diffusion. The rate constant of energy transfer by collisions equals or approximates to that of the bimo-

TABLE 1

The values of  $E_S$ ,  $E_T$  and of molar absorptivity for benzene and ketones investigated

Compound	$E_S$ (kcal/mol)	$E_T$ (kcal/mol)	$\epsilon$ for $\lambda = 254$ nm
benzene	105	84.4	200
aliphatic ketones	~90	~80	~10

lecular process controlled by diffusion. Sometimes the rate constant of sensitization is determined by the efficiency of formation of a loosely bound exciplex between the excited molecule of donor and acceptor molecule during an encounter. A long-range energy transfer, electrostatic in character of dipole-dipole type, is also found. This affects the energy transfer at a distance of 20 - 50 Å [1]. The phenomenon of sensitization generally occurs when the energy values of the singlet  $E_S$  and triplet  $E_T$  states of the sensitizer exceed those of the acceptor. The molar absorptivity,  $\epsilon$ , value of the sensitizer also ought to be much higher than that of the acceptor. The benzene-simple aliphatic ketones systems meet those requirements, which are presented in Table 1. The  $\epsilon$  values for benzene and three ketones: acetone, 2-butanone and 3-pentanone were measured by us and the other values were taken from the literature [14].

In this paper results are given of investigations on the quenching of the excited singlet state of benzene by the above-mentioned ketones and, by way of an example, on the sensitizing effect of benzene upon the degree of photochemical transformation of acetone.

## Experimental

Acetone and 3-pentanone (POCh, Gliwice) were dried with anhydrous  $K_2CO_3$  and distilled twice. Cyclohexane (POCh, Gliwice) was repeatedly washed with concentrated  $H_2SO_4$  until the acid layer no longer turned yellow. The cyclohexane layer was next washed once with distilled water, three times with saturated  $Na_2CO_3$  and three times with distilled water. It was then dried with  $P_2O_5$  and finally fractionally distilled over  $P_2O_5$ , the middle fraction being used. Benzene (E. Merck Darmstadt, AR grade) was purified by the method described by Herkstroeter *et al.* [15]. 2-Butanone (E. Merck, Darmstadt, AR grade), acetonitrile (E. Merck, Darmstadt, AR grade), ethyl acetate (E. Merck, Darmstadt, AR grade) and n-heptane (Carlo Erba, Milan, AR grade) did not need purifying and were used as received. Benzene, all ketones and solvents were checked for purity prior to use by u.v. and fluorescence spectroscopy.

For preparative irradiation we used a double-coated quartz reactor constructed in this laboratory, with thermostating liquid and irradiated liquid,

and a concentrically set Original Hanau 15 W low pressure lamp TNN 15/32 [16]. For quantitative irradiation a "merry-go-round" system was employed. The solutions investigated were irradiated in quartz test-tubes fixed in a rotating support by means of the 4 above-mentioned low pressure lamps arranged symmetrically. The whole was immersed in a water thermostat at a temperature of  $20 \pm 0.5$  °C.

In the preparative investigations the products of acetone photolysis were fractionated on a Pye 105 one-column preparative gas chromatograph using a 1.5 m long column filled with 25% PEGA on 42 - 75 mesh Celite. The quantitative determinations were made on a Pye 104 dual column gas chromatograph using 1.8 m long columns filled with Poropak Q (100 - 120 mesh). The substrates and reaction products were examined spectrophotometrically with a point spectrophotometer of VSU-2P type, Specord UV-VIS type and UR 20 type (Carl Zeiss, Jena) as well as SP-700 type (Pye Unicam). The fluorescence spectra were obtained in 10 mm quartz cells at right angles illumination on a Perkin-Elmer-Hitachi MPF-3 spectrofluorimeter with 150 W xenon lamp source. Spectra were ratio recorded to correct for any fluctuations in source intensity.

## Results and Discussion

The pure benzene and its solutions is known to show fluorescence in the range from 260 to 330 nm [17]. So the decrease in quantum efficiency of benzene fluorescence was found in the presence of the above-mentioned ketones at different concentrations, using cyclohexane, n-heptane, acetonitrile and ethyl acetate as solvents. The quenching constants for particular ketones were calculated from the Stern-Volmer equation:

$$\frac{\Phi_0}{\Phi} = 1 + K_Q [Q]$$

where  $\Phi_0$  = quantum efficiency of benzene fluorescence in the solution in the absence of the ketone,  $\Phi$  = quantum efficiency of benzene fluorescence in the solution containing ketone,  $[Q]$  = ketone concentration in the solution investigated,  $K_Q$  = constant of quenching process of the excited state  $S_1$  of benzene by the ketone (l/mol).

In the calculation of the  $K_Q$  values it was assumed that the respective fluorescent yields are proportional to the areas circled with the fluorescent curves. The ratio of those areas was determined by the method of weighing. Moreover, in calculating the values discussed some allowance was made for partial absorption of the exciting radiation by the ketones and for the absorption of the fluorescent radiation emitted by the benzene. The effect of oxygen upon the lifetime  $\tau_0$  of state  $S_1$  of benzene [18, 19] was also considered, assessing its concentration in the system from values of its solubility. Having the values  $\tau_0$  and  $K_Q$ , the energy transfer rate constant  $k_q$  was calculated from the formula:

TABLE 2

The quenching of benzene fluorescence by the ketones in different solvents ( $\tau_0$  and  $k_{diff}$  values of n-heptane, cyclohexane, acetonitrile and ethyl acetate are respectively:  $\tau_0$ : 5.7; 12.2; 5.7 and 5.7 (ns) and  $k_{diff} \times 10^{-10}$ : 2.4; 1.0; 2.7 and 2.2 ( $l \text{ mol}^{-1} \text{ s}^{-1}$ )).

Quenching ketone	Solvent	$K_Q^{20^\circ\text{C}}$ (l/mol)	$k_q^{20^\circ\text{C}} \times 10^{-10}$ ( $l \text{ mol}^{-1} \text{ s}^{-1}$ )	$k_q/k_{diff}$
acetone	n-heptane	200 $\pm$ 40	3.5 $\pm$ 0.7	1.4 $\pm$ 0.2
	cyclohexane	220 $\pm$ 40	1.8 $\pm$ 0.3	1.8 $\pm$ 0.3
	acetonitrile	250 $\pm$ 50	4.3 $\pm$ 0.9	1.6 $\pm$ 0.3
	ethyl acetate	70 $\pm$ 15	1.2 $\pm$ 0.2	0.6 $\pm$ 0.09
2-butanone	n-heptane	460 $\pm$ 90	8.0 $\pm$ 2.0	3.3 $\pm$ 0.8
	cyclohexane	180 $\pm$ 80	1.5 $\pm$ 0.7	1.5 $\pm$ 0.7
	acetonitrile	210 $\pm$ 10	3.7 $\pm$ 0.2	1.4 $\pm$ 0.1
	ethyl acetate	90 $\pm$ 20	1.6 $\pm$ 0.3	0.7 $\pm$ 0.02
3-pentanone	n-heptane	225 $\pm$ 1	3.9 $\pm$ 0.0	1.6 $\pm$ 0.02
	cyclohexane	120 $\pm$ 50	1.0 $\pm$ 0.4	1.0 $\pm$ 0.4
	acetonitrile	240 $\pm$ 50	4.2 $\pm$ 0.9	1.6 $\pm$ 0.3
	ethyl acetate	100 $\pm$ 20	1.8 $\pm$ 0.4	0.8 $\pm$ 0.02

$$K_Q = \tau_0 k_q \text{ (l mol}^{-1}\text{)}$$

and compared with the rate constants of the bimolecular process controlled by diffusion ( $k_{diff}$ ) in the solvent in question. The results obtained are presented in Table 2.  $k_{diff}$  values given in Table 2 were calculated from the equation of Osborne and Porter [20]:

$$k_{diff} = \frac{8RT}{2000 \eta}$$

where  $R$  is the gas constant,  $T$  is temperature,  $\eta$  is the solvent viscosity (cP).  $\tau_0$  (benzene) in n-heptane, acetonitrile and ethyl acetate was adopted as equal to that in n-hexane. This approximation was taken after a similar assumption made in the literature [19]. Figures 1 - 3 show Stern-Volmer diagrams for the system investigated. The relationship  $\Phi_0/\Phi = f([Q])$  are straight lines from the slope of which the  $K_Q$  values can be calculated.

To give an example here are results of our photochemical investigations on the benzene-acetone-cyclohexane system in order to point out that the transfer of energy is tantamount to its sensitizing effect upon the photochemical reactions of that ketone. The systems and the benzene and acetone concentrations employed here were the same as in the case of investigations on fluorescence. Isopropanol, pinacol, dimethylcyclohexylcarbinol and acetylacetone were revealed in the products of photolysis of acetone in cyclohexane by the method of preparative and analytical gas chromatography, which is also in agreement with previous reports [21, 22]. In quantitative investigations "pure" acetone solutions were exposed and with sensitizer up to about 30% of acetone conversion. Results of chromatographic determination are

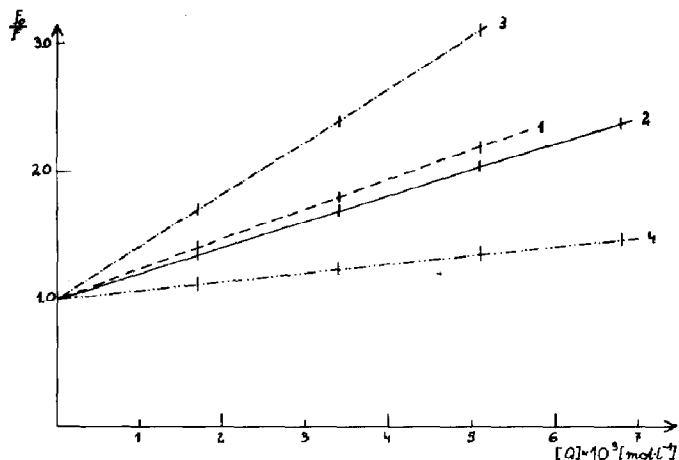


Fig. 1. Stern-Volmer diagram for benzene and acetone solution in cyclohexane (1), n-heptane (2), acetonitrile (3) and ethyl acetate (4).

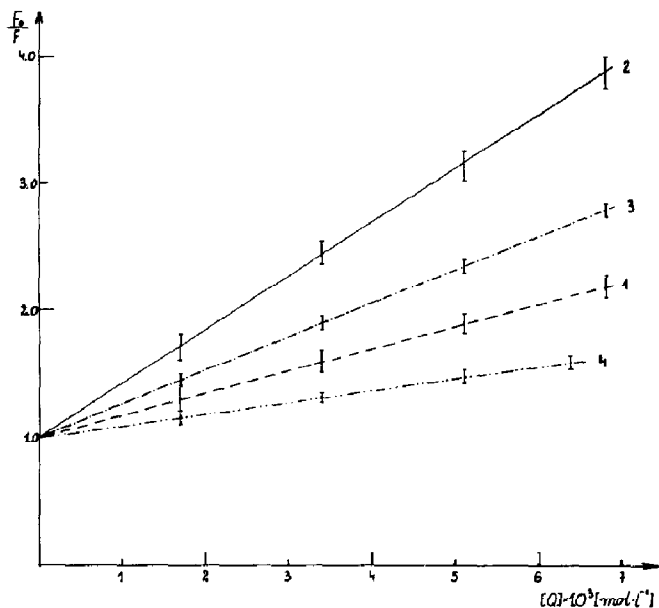


Fig. 2. Stern-Volmer diagram for benzene and 2-butanone solution in cyclohexane (1), n-heptane (2), acetonitrile (3) and ethyl acetate (4).

shown in Fig. 4 where it can be seen that the benzene sensitizes the photochemical decomposition of acetone, which is particularly noticeable in the systems with a lower acetone concentration. Moreover, we have found benzene to sensitize the process of regeneration of acetone from pinacol being one of the photolysis products, which renders the kinetic examination difficult. The data set up in Table 2 show that the value of constants  $k_q$  for all the ketones are higher than those of constant  $k_{diff}$ , of bimolecular processes limited by diffusion. The only exceptions are the solutions in ethyl

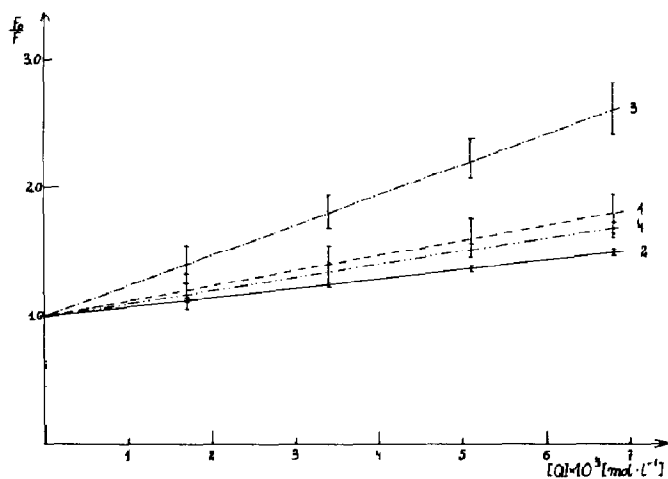


Fig. 3. Stern-Volmer diagram for benzene and 3-pentanone solution in cyclohexane (1), n-heptane (2), acetonitrile (3) and ethyl acetate (4).

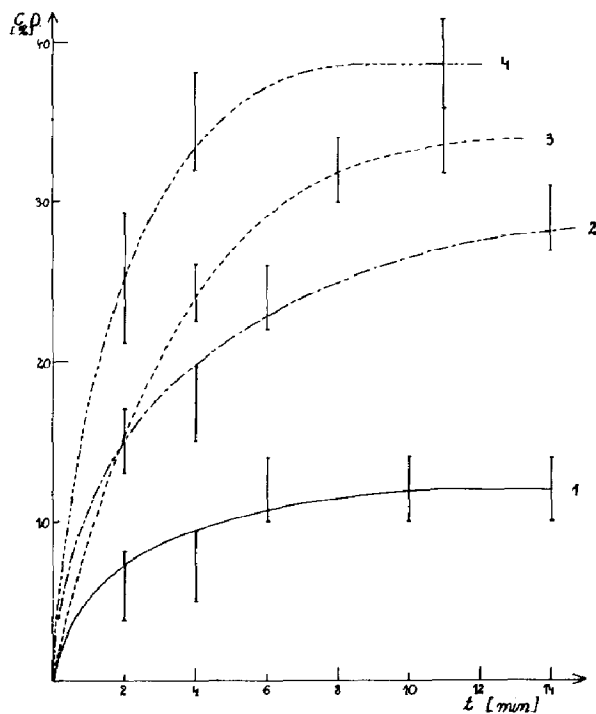


Fig. 4. The conversion degree of acetone at primary concentrations  $c_0 = 6.8 \times 10^{-3}$  mol/l (1 and 2) and  $c_0 = 3.4 \times 10^{-3}$  mol/l (3 and 4) vs. irradiation time with sensitizer (2 and 4) and without it (1 and 3).

acetate. It was found, moreover, that the  $k_q$  values for each ketone decrease as the viscosity of the solvent increases, with the exception of ethyl acetate, in which the fluorescence quenching was investigated. On the grounds of the above data an explicit statement can be made that the mutual diffusion of

benzene and that ketone is decisive for the energy transfer rate of electronic excitation in the system studied. It does not seem, however, to be the only way of passing the excitation. There is some information available about the energy transfer in gaseous phase between aromatic compounds and ketones by long-range effect of dipole type [23]. We think that in our case it can in all probability be stated that the value of  $k_q/k_{diff}$  ratio greater than one results from a dipole-dipole interaction between excited state  $S_1$  of benzene molecule and unexcited ketone molecule.

Further research work aimed at gaining better knowledge of the mechanisms in these systems is continuing.

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