

## MECHANISM OF S<sub>1</sub> DEACTIVATION IN ALKANES: HEAVY-ATOM EFFECT†

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(Received February 8, 1985; in revised form April 14, 1985)

### Summary

We have observed that the fluorescence decay rate of alkanes is sensitive to the presence of xenon. Of the two terms in the decay rate constant, one is temperature independent and the other is thermally activated, only the first being subject to this heavy-atom effect. Therefore it is concluded, in agreement with a previous assignment, that the temperature-independent decay is due to intersystem crossing and the thermally activated decay is due to internal conversion.

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### 1. Introduction

The photophysical properties of saturated hydrocarbons have been extensively studied in the last decade, especially by Lipsky and coworkers, and can be summarized as follows: (i) the fluorescence spectra are broad and structureless and show a large Stokes shift [1 - 3]; (ii) at room temperature the fluorescence quantum yields  $\Phi_f$  are less than  $10^{-2}$  [2, 3] and the fluorescence lifetimes  $\tau$  are approximately equal to 1 ns [4 - 9]; (iii) the deactivation of S<sub>1</sub> leads to molecular photodecomposition with roughly unit quantum yield [10 - 12].

These properties are quite different from those of unsaturated hydrocarbons and reflect the local nature of the electronic wavefunctions and valence excitations in these compounds.

The mechanisms of S<sub>1</sub> deactivation of alkanes have been explored by measuring the decay rate constant  $k = 1/\tau$  as a function of temperature  $T$  for a number of systems [8, 13, 14]. All the compounds examined show a decay rate  $k(T)$  which can be accurately represented by

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†Presented in part at the XVI Informal Conference on Photochemistry, Harvard University, Cambridge, MA, 20 - 24 August, 1984.

$$k(T) = k_0 + A \exp(-\Delta E/RT) \quad (1)$$

where the constant term  $k_0 \approx 10^7 - 10^8 \text{ s}^{-1}$ , the pre-exponential factor  $A$  of the activated term is approximately  $10^{11} - 10^{12} \text{ s}^{-1}$  and the activation energy  $\Delta E \approx 4 \text{ kcal mol}^{-1}$ . The only exceptions to this behaviour were *cis*- and *trans*-decalin, for which  $A \approx k \approx 10^8 \text{ s}^{-1}$ . Similar behaviour, with  $k(T)$  consisting of an activated term and a constant term, was also found for cyclohexane by Wickramaaratchi *et al.* [15].

By comparing the values of  $k_0$  and  $A$  obtained for the alkanes under study with those predicted using the theory of radiationless transitions [16] for internal conversion (IC) and intersystem crossing (ISC) we were able to assign the processes responsible for  $S_1$  deactivation.

Since  $k_0$  is of the order of  $10^8 \text{ s}^{-1}$  and  $A$  has a value of up to  $10^{12} \text{ s}^{-1}$ , the constant term and the activated term have been attributed to ISC and IC respectively [8, 13, 14].

The relative weights of the two decay mechanisms depend, as do other photophysical properties, on the structure of the alkane: at room temperature linear hydrocarbons decay predominantly by the activated IC process, while compounds with tertiary carbon atoms undergo predominantly ISC; in decalins the decay is due entirely to ISC [14].

To confirm this assignment, we have now determined the external heavy-atom effect produced by dissolved xenon on the photophysical parameters  $k_0$  and  $A$  of a selected group of alkanes. As was first observed by Kasha [17], heavy atoms typically increase the rate of spin-forbidden processes (such as phosphorescence and  $S_1 \rightsquigarrow T_1$  and  $T_1 \rightsquigarrow S_0$  ISC) by increasing the spin-orbit coupling. Spin-allowed processes remain essentially unchanged. If our assignment is correct, we would expect that  $k_0$ , but not  $A$ , should increase upon adding xenon to the pure hydrocarbon liquid. In this paper we report the results of these measurements.

## 2. Experimental details

The alkanes, which are commercially available, were passed twice through a 50 cm column of freshly activated silica gel and then their purity was checked spectroscopically. All samples were sealed under vacuum in 1 cm Suprasil fluorescence cells.

The excitation source was a pulsed nitrogen laser (Lambda Physik, Göttingen) with about 3.5 ns full width at half maximum and 1 MW pulse power. Focusing the laser beam on the sample cell produced a two-photon excitation [7]. The emission was detected close to  $\lambda_{\text{max}}$  with a Hamamatsu R955 photomultiplier with a five dinode chain configuration to obtain a fast time response.

Data were acquired by using a Tektronix R7912 transient digitizer equipped with a 7A19 vertical amplifier interfaced to a Z80-based Cromemco microcomputer. Lifetimes were obtained by a deconvolution of the average of five measurements, the scatter being less than 7%.

Low temperatures were maintained with a liquid-nitrogen flow cryostat, whereas temperatures above 283 K were produced by maintaining a flow of water through the sample holder.

Further details on the lifetime measurements have been described previously [14].

Samples of pure liquid alkanes were saturated with xenon gas at a pressure of 1 atm at a temperature  $T = 295$  K. In the cell the volume of the liquid phase was about 10 times that occupied by the xenon gas. This ensures, as discussed below, that upon lowering the temperature the amount of xenon transferred from the gas phase to the liquid phase is negligible.

### 3. Results and discussion

The molecules studied are methylcyclohexane (MC), *cis*-1,3-dimethylcyclohexane (DMC), *cis*-decalin (D) and *n*-pentadecane (P). These were selected as being representative of classes of compounds previously investigated, namely linear chains, alkyl-substituted cyclohexanes and decalins.

The solubility of xenon in these alkanes was evaluated as follows. The Ostwald solubility coefficients have been determined for MC [18] and P [19] and were found to be 4.6 and 3.18 respectively at  $T = 295$  K. From these values, the concentration of xenon at 295 K and 1 atm was calculated to be 0.19 M and 0.13 M for MC and P respectively. Since the solubility of another noble gas, krypton, was found to be relatively insensitive to the structure of the alkane [18], we assumed the solubility in MC and D to be the same as in MC.

Since  $C_l/C_g \approx 4.6$  at room temperature and in the cell the gas volume is less than 10% of the liquid volume, the amount of gas-phase xenon is about 2% of that dissolved in the alkane. On lowering the temperature,  $C_l/C_g$  increases [18]; however, owing to the small fraction of the xenon present in the gas phase,  $C_l$  will remain practically constant over the temperature range considered.

The concentration of xenon appears to be sufficiently high to affect the photophysical parameters of the alkanes. The fluorescence decay times of xenon-saturated alkanes were measured at several temperatures from 310 K to the glass temperature. The results are plotted against temperature in Fig. 1. By comparing these curves with those of the same alkanes in the absence of xenon (also shown in Fig. 1) a shift of  $k(T)$  towards higher values is noticed. Thus, xenon does increase the decay rate constant for all the alkanes considered at all temperatures.

The  $k(T)$  curves of Fig. 1 were analysed using eqn. (1) by a non-linear iterative least-squares fitting procedure [20]. In such a procedure,  $k_0$  and  $A$  were extracted while  $\Delta E$  was fixed to its value for neat alkanes because it was expected to be unaffected by the addition of xenon. The results are reported in Table 1 together with the corresponding values for neat alkanes.

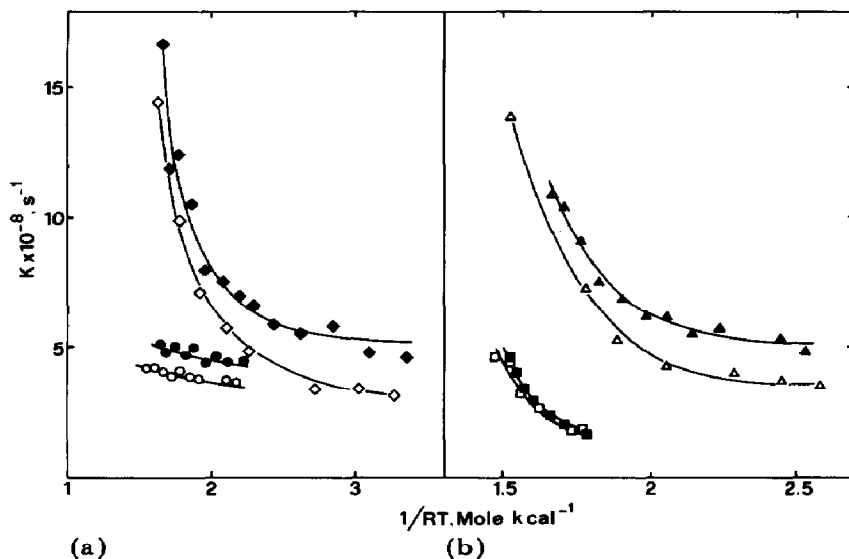


Fig. 1. Decay rate constant  $k$  for  $S_1$  of alkanes plotted vs.  $1/RT$ . Full symbols refer to xenon-saturated samples; open symbols refer to neat alkanes sealed under vacuum. (a)  $\circ$ , D;  $\diamond$ , MC; (b)  $\triangle$ , DMC;  $\square$ , P.

TABLE 1

Pre-exponential factor  $A$ , activation energy  $\Delta E$  and temperature independent term  $k_0$ , obtained without xenon and with xenon

Compound	Under vacuum			Xe		
	$A^a$ ( $s^{-1}$ )	$\Delta E^b$ (kcal mol $^{-1}$ )	$k_0^a$ ( $s^{-1}$ )	$A^a$ ( $s^{-1}$ )	$\Delta E^b$ (kcal mol $^{-1}$ )	$k_0^a$ ( $s^{-1}$ )
D	$5.0 \times 10^8$	0.9	$3.0 \times 10^8$	$6.5 \times 10^8$	0.9	$3.5 \times 10^8$
P	$1.0 \times 10^{12}$	5.2	$8.0 \times 10^7$	$7.9 \times 10^{11}$	5.2	$1.0 \times 10^8$
MC	$7.5 \times 10^{11}$	3.9	$3.4 \times 10^8$	$6.7 \times 10^{11}$	3.9	$5.2 \times 10^8$
DMC	$2.0 \times 10^{12}$	4.8	$3.6 \times 10^8$	$1.7 \times 10^{12}$	4.8	$5.1 \times 10^8$

<sup>a</sup> $k_0$  is subject to an error of 10% or less, while the error in  $A$  is 100% or less.

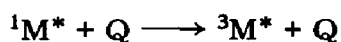
<sup>b</sup> $\Delta E$  is assumed to be insensitive to the presence of xenon.

The parameter  $k_0$  is found to increase in all the compounds. In the cyclohexane derivatives MC and DMC the increase is  $1.8 \times 10^8 s^{-1}$  and  $1.5 \times 10^8 s^{-1}$  respectively. In D, as discussed previously, the distinction between unactivated and activated decay is meaningless, since here  $A$  is similar in value to  $k_0$  and both constants describe the same type of decay. Thus, in this case it is more appropriate to consider only the change in  $k = 1/\tau$ . The increase in  $k$  is about  $0.8 \times 10^8 s^{-1}$  and is roughly independent of temperature. The increase in  $k_0$  for P of about  $0.2 \times 10^8 s^{-1}$  is the smallest, perhaps because the solubility of xenon is lowest in this case.

The small decrease in the pre-exponential factor  $A$  probably has no physical significance, but we believe that the observed increase of  $k_0$  in the

presence of xenon is real. This confirms our previous assignment of  $k_0$  to ISC and of  $A \exp(-\Delta E/RT)$  to IC because of the correlation between decay mechanism and type of photodecomposition proposed previously [14]; it also suggests that the yield of the radical photoproduct will increase on the addition of xenon.

It is worth noting the constancy of the heavy-atom effect on  $k_0$  in the temperature range where it can be determined accurately. In fluid solutions the dominant mechanism of heavy-atom quenching of fluorescence is generally attributed to the formation of an exciplex  ${}^1E^*$  followed by enhanced ISC  ${}^1E^* \rightsquigarrow {}^3E^*$ , as was originally suggested by Kasha [17]. Direct evidence for this is provided by the experiments of Wilkinson [21] which show that the overall process



(where Q is the heavy atom) is collisional and is well described by a Stern-Volmer equation. It has also been observed that the  $S_1 \rightsquigarrow T_1$  ISC rate is far more influenced by heavy atoms than either the rate of phosphorescence or that of the  $T_1 \rightsquigarrow S_0$  process [22]; moreover, theoretical arguments have been presented to explain such behaviour [23].

Assuming that the collisional mechanism is dominant in the present case through the range of temperatures studied, we have for  $k_0$ :

$$k_0(C_X) = k_0 + k_q C_X \quad (2)$$

where  $k_q$  is the quenching rate constant. Applying this equation to the MC data ( $C_X = 0.19$  M,  $\Delta k_0 = 1.8 \times 10^8$  s<sup>-1</sup>), we estimate  $k_q \approx 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The quenching rate  $k_q$  is controlled by the diffusion rate  $k_d$  and by the  $S_1 \rightsquigarrow T_1$  ISC rate  $k_E$  in the exciplex. In fact, the following relation is approximately valid [24].

$$k_q = \frac{k_d k_E}{k_{\text{diss}} + k_E} \quad (3)$$

where  $k_{\text{diss}}$  is the rate for the dissociation of the encounter complex. Equation (3) implies that the observed quenching rate  $k_q$  is a lower limit both for  $k_d$  and  $k_E$ . In particular we have  $k_d > 10^9$  s<sup>-1</sup> M<sup>-1</sup> down to 150 K. This suggests that the diffusion rate of xenon in MC has a very low temperature dependence, at variance with the Stokes-Einstein relation  $k \propto T/\eta$  [25]. The deviation from Stokes-Einstein behaviour can be explained in terms of the Gierer-Wirtz theory [26] and is larger when the molar volume of solute is smaller than that of the solvent [24]. In such a case the solute can migrate into pre-existing holes in the solvent; the energy required for such motion was found to be less than 20% of the activation energy of viscous flow for liquids like hydrocarbons [27]. In the present case the radius of the solute (2.7 Å) is smaller than that of the solvent (greater than 3.7 Å) for the four compounds studied; thus the diffusion of the solute takes place mainly by migration into the solvent holes without requiring an appreciable activation energy. This may explain why the heavy-atom effect appears to be indepen-

dent of temperature. To test these conclusions, it would be helpful to have data corresponding to several concentrations of xenon. In fact possible contributions from non-diffusional processes could result in deviation from Stern-Volmer kinetics [28]. Unfortunately the present accuracy in the determination of  $C_0$  and the fluorescence decay does not allow the problem to be considered properly.

Finally it can be observed in Fig. 1 that the  $k(T)$  curve of DMC shows a small irregular bump at low temperatures close to the glass temperature which seems to be related to a change in the alkane liquid structure.

#### 4. Conclusions

We conclude that addition of xenon to the neat alkanes increases the decay parameter  $k_0$  but not the pre-exponential factor. This confirms the assignment of the process described by  $k_0$  to ISC and the process whose rate is  $A \exp(-\Delta E/RT)$  to IC.

The heavy-atom effect is independent of temperature and remains large even at low temperatures. Since the mechanism of this effect requires exciplex formation, the above observation agrees with the theory that xenon mainly diffuses into already-existing holes in the solvent.

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