INTRAMOLECULAR PHOTOCHEMICAL HYDROGEN ABSTRACTION RATES IN DOUBLY ANCHORED ALKANE CHAINS

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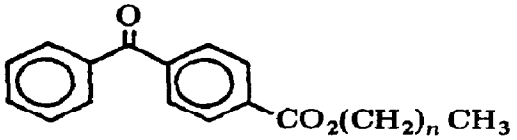
Summary

In this paper we report the results of laser flash photolysis experiments on a series of molecules containing alkane chains. It is found that the rate of intramolecular hydrogen abstraction for molecules whose polymethylene chain is anchored at both ends is 10 - 100 times faster than for molecules whose chain is attached at one end only. The difference in reactivity is discussed in terms of the number of accessible chain conformations.

1. Results and discussion

Intramolecular phosphorescence and fluorescence quenching have been used to study the conformation of oligomeric and polymeric flexible chain species [1 - 4]. In most of these experiments, the kinetics of interaction were studied between an electronically excited chromophore at one chain end and a quencher at the other end, *i.e.* molecules of the form A*...Q [1, 2]. In other experiments, the kinetics were studied of a chemical reaction between the excited chromophore and groups along the chain [3, 4]. For example, in 1



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the rate at which the ketone in its triplet state abstracts a hydrogen from the CH_2 groups of the polymethylene chain gives a measure of the probability that the CH_2 group is adjacent to the carbonyl oxygen. This rate constant k_{1H} can be related to the cyclization probabilities of each of the CH_2 groups in the chain [3 - 5].

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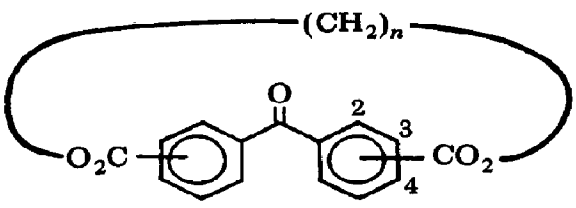
In molecules such as 2

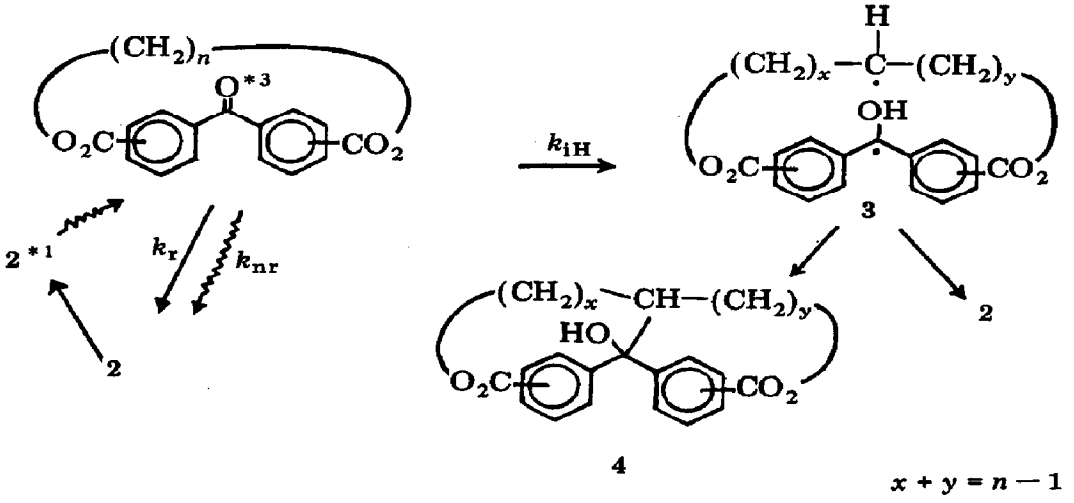


2a ≡ 3,3′
2b ≡ 3,4′
2c ≡ 4,4′

the chain is anchored at both ends. This constrains the number of conformations accessible to the chain and should have a strong influence on the magnitude of k_{iH}. Here we report laser flash photolysis experiments on a series of molecules of the general structure 2 (n = 16, 18, 20, 22) which permit values of k_{iH} to be calculated. These values are interpreted in terms of factors which affect chain conformation in these molecules.

The molecules 2 were prepared by the German group. The syntheses and their characterization will be reported elsewhere. Dilute samples (1×10^{-3} M) of each substance in carefully purified carbon tetrachloride [6] were placed in cylindrical Pyrex tubes and sealed under vacuum after five successive freeze–pump–thaw cycles. These samples, at 22 °C, were excited by pulses of a nitrogen laser. Phosphorescence signals were detected at $\lambda > 400$ nm at 90° to the incident light. Typically 20 decay traces were averaged so that two decades (99%) of the emission decay could be followed. Decays were cleanly exponential. Lifetimes among samples were reproducible (typically, ±3%). Nevertheless, all long-chain samples were degassed simultaneously with the corresponding dimethyl ester 2(1) (n = 1) in the same batch of purified solvent.

The main processes of the depopulation of the triplet state of each sample can be expressed by the following scheme:



$x + y = n - 1$

Intramolecular phosphorescence quenching by CH_2 groups of the chain occurs by hydrogen abstraction, described by k_{iH}. The ketone triplet can also decay by radiative and non-radiative pathways ($k_r + k_{nr}$) characteristic of the chromophore. The data analysis presumes that ($k_r + k_{nr}$) is the same for the corresponding dimethyl ester (τ_{Me}^{a} describes 2a(1)):

$$\frac{1}{\tau_{Me}^{a,b,c}} = (k_{nr} + k_r)_{a,b,c} \tag{1}$$

Consequently k_{iH}, for each series of substituted benzophenones, can be calculated by comparing the lifetimes of the long chain and dimethyl esters according to

$$k_{iH}^{a,b,c} = \frac{1}{\tau_2^{a,b,c}} - \frac{1}{\tau_{Me}^{a,b,c}} \tag{2}$$

The results of our experiments are shown in Table 1 and Fig. 1.

We note first of all that the triplet lifetimes of 2a, 2b and 2c are significantly different, with the 4,4′ compound having the longest lifetime, and the 3,3′ compound having the shortest. By comparison, 4-carboxymethylbenzophenone, in this batch of solvent, has a lifetime of 57 μs. The origin of these differences is not yet clear. Further work is necessary to determine whether both k_r and k_{nr} are affected.

The most striking feature of the data in Fig. 1 is the effect of substitution pattern on the rate of intramolecular hydrogen abstraction.

TABLE 1

Experimental results

Sample	*Chain length* n	k_{iH} ($\times 10^4$ s^{-1})	$k_H^{(2)}$ [a] ($\times 10^6$ M^{-1} s^{-1})	C_0 [b] (M)
2a(22)	22	26.6		1.35
2a(18)	18	27.4		1.39
2a(16)	16	23.1		1.17
2a(1)			1.18	
2b(22)	22	21.8		1.15
2b(20)	20	25.3		1.33
2b(18)	18	19.4		1.02
2b(1)			1.14	
2c(22)	22	6.53		0.344
2c(20)	20	8.05		0.424
2c(18)	18	3.82		0.201
2c(1)			1.14	

Structure: a compounds, 3,3′; b compounds, 3,4′; c compounds, 4,4′.

[a] Bimolecular rate constant for triplet quenching by *n*-octane.

[b] Effective concentration per CH_2 group: $C_0 = 6k_{iH}/k_H(2)$.

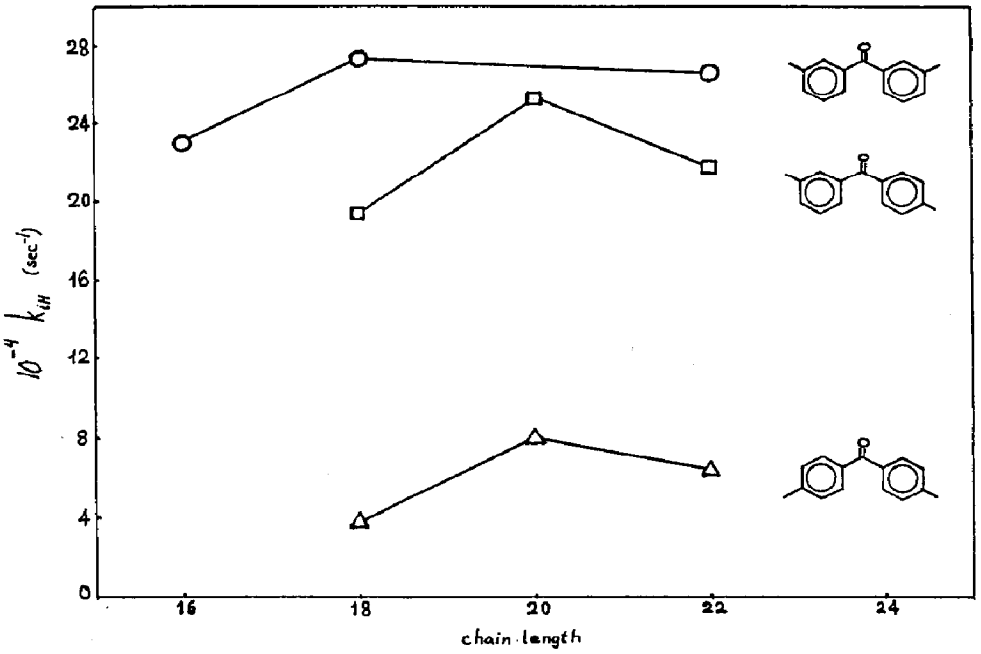


Fig. 1. Plot of the intramolecular hydrogen abstraction rate constant as a function of the number of CH_2 groups for **2a** (○), **2b** (□) and **2c** (△).

Within each series of benzophenone derivatives, very similar intramolecular quenching rates are found. This quenching is undoubtedly due to hydrogen abstraction. The obvious interpretation is that a small variation in the number of CH_2 groups in the chain does not have a large effect on the fraction of chain conformations which place a hydrogen atom from a CH_2 group within a reactive distance of the ketone oxygen. The small differences noted, which seem to favour reaction when $n = 20$, reflect very small differences in the population of reactive conformations compared with unreactive conformations for each molecule.

The differences in reaction rates between the 3,3′-, 3,4′- and 4,4′-substituted molecules may be due to differences in the fraction of reactive chain conformations or to differences in the intrinsic reactivity of the individual benzophenone groups. In order to compare these individual reactivities, we carried out model studies, examining the ability of *n*-octane to act as a quencher for the triplet states of **2a(1)**, **2b(1)** and **2c(1)**. Octane quenches ketone $n\pi^*$ triplet states by hydrogen abstraction. The CH_2 groups in octane are substantially more reactive than the methyl groups, and each contributes equally to the reaction [6]. The second-order quenching rate constants $k_H^{(2)}$ can therefore be converted to a rate constant $k_{CH_2}^{(2)}$ per CH_2 group simply by dividing $k_H^{(2)}$ by six.

Values of $k_H^{(2)}$ were obtained by Stern–Volmer analysis

$$\frac{1}{\tau_{Me}} = \frac{1}{\tau_{Me}^0} + k_H^{(2)}\,[\text{octane}] \qquad (3)$$

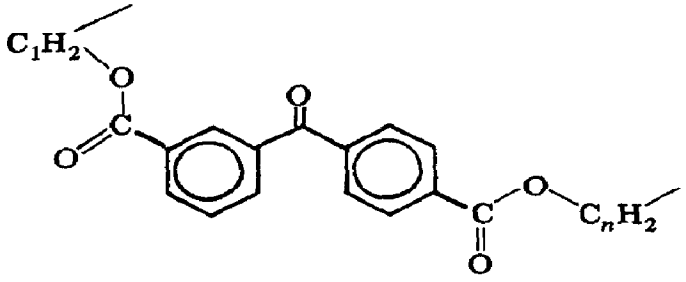
of the triplet lifetimes of each ketone 2(1) as a function of octane concentration. The data in each case gave linear plots and interestingly, essentially identical values of $k_H^{(2)} = 1.2 \times 10^6\ M^{-1}\ s^{-1}$ for each derivative. This result means that the triplet states of 2a(1), 2b(1) and 2c(1) are equally reactive towards hydrogen abstraction, and are characterized by a value of $k_{CH_2}^{(2)} = 2.0 \times 10^5\ M^{-1}\ s^{-1}\ (CH_2)^{-1}$.

The values of $k_{CH_2}^{(2)}$ can be used to normalize the k_{iH} results, permitting the effective concentration C_0 to be calculated [7].

$$C_0 = \frac{k_{iH}}{k_{CH_2}^{(2)}} \tag{4}$$

C_0 is proportional to the probability that a CH_2 group in 2a, 2b or 2c can achieve a reactive conformation. C_0 values are about 0.2 - 0.4 M for 2c with 4,4′ substitution and about 1 M for 2a and 2b. These are an order of magnitude larger than in 1 ($C_0 = 0.04$ M for 1 ($n = 12$) [3]) where the chain is attached at only one end, at the 4-position of the benzophenone.

The increase in C_0 associated with anchoring the other chain end is easily explained. C_0 is equal to the ratio of the (energy-weighted) number of reactive chain conformations to the total number of chain conformations. Computer simulations [5] estimate of the order of 10^4 discrete conformations of 1 ($n = 12$), where each bond of the chain is in the gauche or trans rotational state, with successive $g^{\pm}g^{\mp}$ pairs not permitted. Tying down both ends of the chain, as in 2, decreases the total number of chain conformations to a number of the order of 10^2:



ester groups trans in 2b

With both ends of the chain constrained there are also changes in the number of reactive conformations. These depend sensitively on the points of chain attachment to the ring. For these short chains which barely span the space between the two ester groups, torsional distortions of the chain, the ester groups and the aromatic ring can contribute to the reaction in ways that are beyond the features of the simple model described in the preceding paragraph. Nonetheless we explain the increase in C_0 in terms of a small decrease in the number of reactive conformations of the chain coupled with a much larger decrease in the total accessible chain conformations.

We do note from inspection of molecular models that, for the 4,4′-substituted molecule with $n = 18$, reactive geometries cannot be reached if

the ester groups are trans coplanar with the attached ring, and if the benzophenone is held nearly planar. Twisting one phenyl group out of the plane enhances the proximity of the ketone C=O and chain CH_2 groups. Also effective is a cis ester group conformation. The energy requirements for these distortions are largely unknown. Presumably some insight would be gained from a knowledge of the temperature dependence of k_{iH} compared with that of $k_H^{(2)}$.

2. Conclusion

Intramolecular hydrogen abstraction in the molecules 2, with a polymethylene chain anchored at both ends, is 10 - 100 times faster than in 1 where the chain is attached at only one end. The reactivity difference is not due to an enhanced reactivity of the benzophenones bearing two electron-withdrawing substituents. Rather, it reflects a large decrease in the number of accessible chain conformations so that a large fraction of these place a CH_2 group in a reactive position next to the ketone C=O.

3. Experimental details

The molecules 2 were prepared and characterized by the Münster group and will be described in a separate publication.

Solutions of 2 (1×10^{-3} M) in carefully purified carbon tetrachloride [3, 4, 6] were placed in cylindrical Pyrex cells (13 mm (outside diameter) × 50 mm) fitted with a joint and attached to a vacuum line. They were sealed under vacuum after five freeze–pump–thaw cycles. Some tubes were heated subsequently overnight at 45 °C to redissolve the sample.

Phosphorescence lifetimes were measured in an apparatus which has previously been described in detail [6]. A nitrogen laser served as an excitation source. Emission was detected at right angles and the transients were digitized by a Biomation 8100 waveform recorder. These were transferred to a Tektronix 4052 microprocessor where the signals were averaged (10 - 20 decay traces) and fitted to an exponential form. Values of τ were reproducible to ±3% for different samples of the same material. The precision of k_{iH} values is estimated at ±5%.

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