

THE PHOTOREACTION OF POLY(ETHYLENE GLYCOL)S WITH AN AROMATIC KETONE: CHAIN LENGTH AND TEMPERATURE EFFECTS ON HYDROGEN ABSTRACTION KINETICS

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Summary

The lowest triplet state of 4-carbomethoxybenzophenone reacts with poly(ethylene glycol) oligomers in acetic acid solution by a hydrogen abstraction mechanism. The rate constant for this reaction is five times larger for CH_2OC groups than for CH_2OH groups. The former reaction is characterized by $E_a = 3.7 \text{ kcal mol}^{-1}$, whereas for the latter $E_a = 5.0 \text{ kcal mol}^{-1}$. For higher homologues of poly(ethylene glycol) at 25°C , the second-order rate constant takes the value $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} (\text{CH}_2)^{-1}$.

1. Introduction

Several years ago Schnabel and coworkers [1] used pulse radiolysis techniques to look at the reaction of $\cdot\text{OH}$ radicals with poly(ethylene oxide). This particular hydrogen abstraction reaction is almost diffusion controlled. Schnabel and coworkers observed that the second-order rate constant $k_{\text{H}}^{(2)}$ for this reaction increases linearly with the mean squared radius of gyration of the polymer. The picture that emerges from their work is that upon encounter of $\cdot\text{OH}$ with the polymer coil the $\cdot\text{OH}$ is essentially "swallowed up" by the polymer and the rate constant for the reaction increases with the effective hydrodynamic radius of the polymer presented to the diffusing $\cdot\text{OH}$ radical.

Quite a different dependence of the second-order rate constant for hydrogen abstraction is observed when this reaction is inefficient [2]. For example, benzophenone in its excited triplet state reacts with alkanes, and only 1 in 10^5 encounters results in hydrogen abstraction [2, 3]. Under these circumstances the excited ketone can enter and depart from the neighbourhood of the alkane many times before reacting. Here $k_{\text{H}}^{(2)}$ increases linearly with the number of CH_2 groups in the chain [2]. This result implies that $k_{\text{H}}^{(2)}$ is insensitive to the length of the hydrocarbon chain but depends only on the bulk concentration of CH_2 groups in solution.

In order to examine the generality of this conclusion, we examined the kinetics of a hydrogen abstraction reaction between the aromatic ketone 4-carbomethoxybenzophenone (K) and a series of poly(ethylene oxide) oligomers. The rate constants were obtained as a function of temperature. We show that the $\text{CH}_2\text{—OH}$ groups at the chain ends are less reactive than the $\text{CH}_2\text{—O}$ groups in the chain interior and that this lower reactivity derives from a larger activation energy. For longer chains $k_{\text{H}}^{(2)}$ increases linearly with the number of interior $\text{CH}_2\text{—O}$ groups, and this effect derives from a more favourable entropy of activation.

2. Experimental details

Ethylene glycol, di(ethylene glycol), tri(ethylene glycol) and tetra(ethylene glycol) were purchased from Aldrich. Penta(ethylene glycol) and hexa(ethylene glycol) were purchased from the Fairfield Chemical Co. These reagents were fractionally distilled at reduced pressure and analysed by gas-liquid chromatography (GLC). Details of these procedures are given in Table 1. The ketone K was prepared and purified as described previously. The acetic acid was refluxed over chromium trioxide and distilled [4].

Six samples containing 1.0×10^{-3} M K and six different concentrations of each poly(ethylene glycol) were prepared. These concentrations ranged from 0.01 to 0.4 M for ethylene glycol and from 0.001 to 0.01 M for hexa(ethylene glycol). The range of concentrations were chosen to give a reasonable extent of quenching of the ketone phosphorescence after excitation. 3 ml of each solution were placed in sample cells made from Pyrex tubing with an outside diameter of 13 mm. These were rigorously outgassed by five freeze-pump-thaw cycles and sealed under a vacuum of at least 10^{-5} Torr.

The samples were subjected to flash photolysis using techniques previously described [2, 3]. The ketone phosphorescence decays were

TABLE 1

Boiling point and gas chromatographic data for $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

<i>n</i>	Boiling point pressure (°C)	GLC column ^a	Flow rate (ml min ⁻¹)	Temperature (°C)	Retention time (min)
1	67 (1 mm)	A	50 (N ₂)	240	2.28
2	93 (0.5 mm)	A	50 (N ₂)	240	8.75
3	93 (25 μm)	A	60 (He)	245	29.7
		B	30 (N ₂)	220	0.83
4	103 (90 μm)	B	30 (N ₂)	220	1.63
5	143 (80 μm)	—	—	—	—
6	153 (25 μm)	—	—	—	—

^aA, 5 ft × 0.25 in, Porapak Q; B, 6 ft × 0.125 in, OV 101 on Chrom G (HP) 60/80 mesh.

exponential with decay times τ . These could be fitted at all temperatures to the modified Stern-Volmer equation

$$\frac{1}{\tau} = \frac{1}{\tau^0} + k_H^{(2)}[Q] \quad (1)$$

where $[Q]$ (quencher) is the poly(ethylene glycol) concentration and τ^0 is the lifetime of K^{*3} in the absence of glycol.

3. Results and discussion

Figure 1 shows a plot of τ^{-1} versus $[Q]$ for tri(ethylene glycol) in acetic acid at six temperatures between 4 and 60 °C. At all temperatures, linear plots according to eqn. (1) are observed. Both the slopes and the intercepts increase with increasing temperature. The slopes are equal to the second-order rate constants for hydrogen abstraction $k_H^{(2)}$ at each temperature. At 25 °C $k_H^{(2)}$ has a value of $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, much less than would indicate diffusion control. The increase in $k_H^{(2)}$ with increasing temperature reflects the activation energy barrier for this reaction. The intercepts give $(\tau^0)^{-1}$ values. While these values are not central to the question of oligomer reactivity, they do reflect the reactivity of K^{*3} with the solvent [4]. This rather slow reaction is probably a hydrogen abstraction from the CH_3 group of acetic acid, retarded by the electron-withdrawing effect of the adjacent carbonyl group.

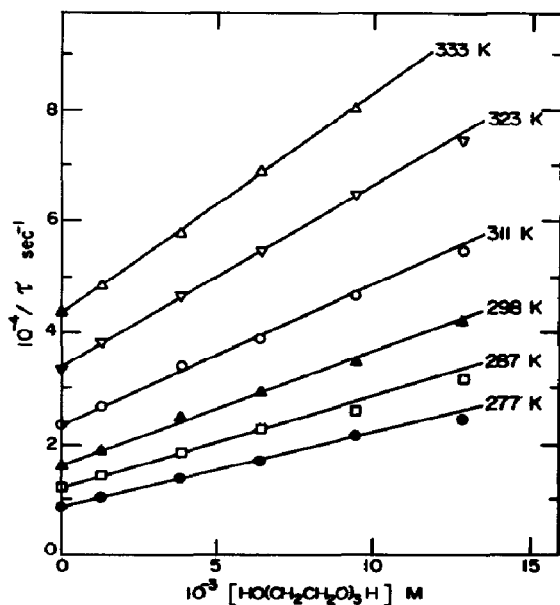


Fig. 1. Plot of $1/\tau$ vs. $[Q]$ for the reaction of K^{*3} with tri(ethylene glycol) in acetic acid at six temperatures between 4 and 60 °C.

Figure 2 presents a plot of $k_H^{(2)}$ versus n for $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. For $n > 1$, $k_H^{(2)}$ increases linearly with the chain length and the line extrapolates to zero at $n = 1$. This implies that the penultimate CH_2 groups adjacent to the terminal OH groups are significantly less reactive than the internal methylenes in the poly(ethylene glycol)s. In ethylene glycol itself, $k_H^{(2)}$ is not zero. The molecule does react but its value of $k_H^{(2)}$ at 25 °C is less than half that for di(ethylene glycol).

The rate constants at the various temperatures are collected in Table 2 and plotted in an Arrhenius fashion in Fig. 3. From these results we can see that the reactivity difference between the CH_2OH groups and the CH_2OC groups toward hydrogen abstraction is a higher activation energy (of 1.3 kcal mol^{-1}) for the former. The pre-exponential factors for the reactions of ethylene glycol and di(ethylene glycol) are comparable, with the former somewhat favoured.

The hydrogen abstraction reactions of the higher homologues of poly(ethylene glycol) have indistinguishable activation energies. These values (3.7 kcal mol^{-1}) are virtually identical with the activation energies of hydrogen abstraction of benzophenone from n -alkanes [2, 5]. The increasing reactivity of the longer chains is due solely to increasing values of the pre-

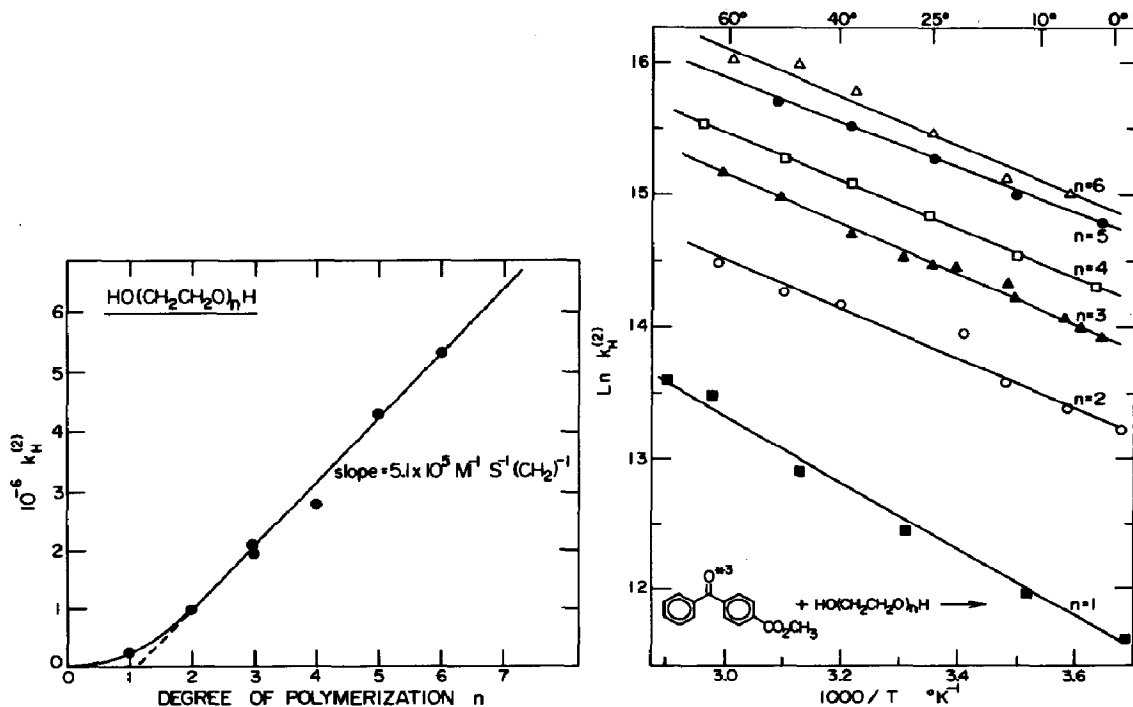


Fig. 2. Plot of $k_H^{(2)}$ (25 °C) vs. n for the reaction of K^*3 with $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ in acetic acid at 25 °C.

Fig. 3. Arrhenius plot of $\ln k_H^{(2)}$ vs. $1/T$ for the reaction of $\text{K}^*3 + \text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ in acetic acid.

TABLE 2

Kinetic data for the quenching of triplet 4-carbomethoxybenzophenone by $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ in acetic acid

n	$k_{\text{H}}^{(2)}$ at 25 °C ($10^6 \text{ M}^{-1} \text{ s}^{-1}$)	ΔE (kcal mol^{-1})	A factor ($\text{M}^{-1} \text{ s}^{-1}$)	Correlation coefficient
1	0.24	5.0 ± 0.3	1.0×10^9	-0.9951
2	1.03	3.7 ± 0.1	5.8×10^8	-0.9979
3	1.98	3.6 ± 0.3	9.0×10^8	-0.9906
4	2.74	3.7 ± 0.1	1.5×10^9	-0.9985
5	4.30	3.6 ± 0.3	1.7×10^9	-0.9815
6	5.29	3.9 ± 0.3	3.9×10^9	-0.9972

exponential factors. This indicates that entropic factors favour the reaction. From the linear portion of the plot in Fig. 2 we calculate a per CH_2 rate constant of $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Consequently we conclude that the rate of reaction of poly(ethylene glycol)s with K^{*3} depends only upon the bulk concentration of $\text{CH}_2\text{—OC}$ groups in solution and not on the details of oligomer chain length or chain dimensions.

It is interesting to compare the relative reaction rates of alkanes and poly(ethylene glycol)s toward hydrogen abstraction, since this is thought to represent one of the key initial steps in polymer photodegradation. Polyethers are more reactive. The per CH_2 rate constant for hydrogen abstraction $k_{\text{CH}_2}^{(2)}$ is a factor of 2.8 larger for $\text{CH}_2\text{—OC}$ groups ($5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) than for alkyl $\text{CH}_2\text{—CH}_2\text{—CH}_2$ groups ($1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).[†] Both reactions have identical activation energies; entropic factors favour the reactivity of the $\text{CH}_2\text{—OC}$ group. In acetic acid solution the per CH_2 reactivity of $\text{CH}_2\text{—OH}$ is $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. It is slightly more reactive than the corresponding alkyl CH_2 group in alkanes despite the activation energy being $1.3 \text{ kcal mol}^{-1}$ higher. Again entropic factors play the dominant role.

It is difficult at this time to pinpoint the origin of these entropic effects as they could arise either from the geometric details of the reactants in the transition state or from contributions of solvent entropy to the reaction rates. Acetic acid is known to enhance several reactions of aromatic ketone triplet states[†], and where these reactions have been examined in sufficient detail the acetic acid seems to affect the activation entropy of the reactions rather than their activation energies [7]. What is not yet clear is whether these effects originate in the polarity of the medium or in its acidity.

[†] Benzophenone*³ reacts with n -alkanes in carbon tetrachloride with $k_{\text{CH}_2}^{(2)}$ (25 °C) = $9.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $E_a = 3.9 \text{ kcal mol}^{-1}$. K^{*3} reacts with alkanes in carbon tetrachloride with $k_{\text{CH}_2}^{(2)}$ (25 °C) = $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $E_a = 3.8 \text{ kcal mol}^{-1}$. At 25 °C acetic acid enhances $k_{\text{CH}_2}^{(2)}$ by a factor of 1.32, i.e. $k_{\text{CH}_2}^{(2)}$ (25 °C) = $1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in acetic acid (see also refs. 6 and 7).

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