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THE KINETICS OF OH RADICAL REACTIONS IN IRRADIATED ORDINARY AND SUPERCOOLED WATER

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INTRODUCTION

Fast reactions are usually regarded as diffusion-controlled processes, while slower ones are expected to have rate constants independent of the rate and activation energy of the diffusion. This classification based on the numerical values of the rate constant has been theoretically criticised [1] and experimentally refuted [2]. As to the latter, Anbar and co-workers, investigating the temperature dependence of the rate constants of hydrated electron reactions, demonstrated that all the reactions had essentially the same energy of activation and that this was equal to the activation energy of diffusion, or in other words that both fast and slow reactions are diffusion-controlled, although their rate constants might differ some five orders of magnitude.

The main purpose of our present investigations was to get some insight into the kinetic nature of the OH radical reactions. We studied the temperature-dependent kinetics of competing OH scavenger reactions and tried to understand our findings in terms of diffusion-controlled processes.

Our second aim was to investigate whether supercooling has any effect, besides that of the change in temperature, on reaction kinetics. Lately we have observed some unexpected effects in the temperature dependence of primary radiation chemical yields during supercooling [3]. This does not, however, either imply or exclude any new phenomenon in kinetics. From a practical point of view the use of supercooled liquids may be advantageous if the system contains thermally unstable or volatile constituents. Experiments carried out in the temperature interval between -8°C and +23°C supplies the same amount of information as those carried out between 23°C and 80°C, in the sense that the two ranges are roughly equal when expressed as the reciprocals of the absolute temperatures.

The reference substance used in most of our experiments was p-nitrosodimethylaniline /PNDA/, which was proved by Kraljic and Trumbore [4] to be a specific scavenger of OH radicals. These authors demonstrated for a series of known OH scavengers that the yield of the decomposition of PNDA obeys simple competition kinetics, i.e. it is given by

$$\frac{1}{G(-\mathrm{PNDA})} = \frac{1}{G_O(-\mathrm{PNDA})}\left(1 + \frac{k_2[S]}{k_1[\mathrm{PNDA}]}\right) \qquad /1/$$

where k_2 is the rate constant of the S+OH and k_1 of the PNDA + OH reaction, respectively. Some further experiments were made with Safranine-T which also has been shown to be selective to OH attack [5].

EXPERIMENTAL

Distilled water was twice redistilled from alkaline permanganate and acid dichromate and used, as a rule, within two days. KBr, KJ, $NaNO_2$ and tartrate were Merck p.a. and were used without further purification. Methanol and ethanol /Reanal p.a./ were triply distilled, PNDA /p-nitrosodimethylaniline/ was prepared by nitrosation of dimethylaniline [6] and was purified by repeated crystallization from ethylether. Stock solutions of PNDA /$5 \cdot 10^{-3}$ M/ were stable for periods up to several weeks when protected from light and stored in a refrigerator. All investigated solutions were air-saturated and adjusted to pH 9 by addition of $Na_2B_4O_7$ solution. Samples were kept at each temperature for half an hour prior to irradiation. No precautions were needed for keeping the solutions perfectly still.

The irradiations were carried out using a 2.000 Ci ^{60}Co γ-source with dose $3.84 \cdot 10^{17}$ ev.ml^{-1} and dose rate $3.84 \cdot 10^{16}$ ev.ml^{-1}.min.$^{-1}$. Temperature stability of the samples during irradiation was maintained by constant temperature baths and was measured as $\pm 0.5^{\circ}$C.

Analyses were made at room temperature. PNDA was measured at 440 mμ /extinction coefficient 34.200/ on a Beckman DU spectrophotometer.

RESULTS

The relative rate constants of PNDA and six different solutes were measured at different temperatures between 23°C and -8°C. The solutes were J^-, NO_2^-, B_r^-, tartrate, methanol and ethanol, all of which have previously been investigated [4]. The usual 1/G versus C_2/C_1 plot is given in Fig. 1. for KBr at two different temperatures. The validity of eq. /1/ both above and below the equilibrium melting point can be seen, i.e. simple competition kinetics prevail also in the supercooled region.

From the slope and intersection of such plots one can determine the ratio of the experimentally observed rate constants /one for each temperature/. We plotted the logarithm of the rate constant ratios against the reciprocal of the absolute temperature, these plots are given in Figs. 2 and 3. A straight line can be reasonably fitted to each series of experimental points. No indication of any break or discontinuity near 0°C can be observed in the plots. The slope of the $\ln\left(k_{2obs}/k_{1obs}\right)$ versus $1/T$ plot is usually regarded as a measure of the difference in the activation energies of the two competing reactions ; i.e. slope = $-\left(\varepsilon_{2obs} - \varepsilon_{1obs}\right)/R$. The observed rate constant ratios and activation energy differences are given in Table I. All the values were computed by the least square method.

Table I

Rate constant ratios and activation energies differences of S+OH reactions relative to the PNDA+OH reaction

S	k_{2obs}/k_{1obs}	$\varepsilon_{2obs} - \varepsilon_{1obs}$ (Kcal/M)
J^-	1.22	0.7 ± 0.3
NO_2^-	0.86	-1.0 ± 1.0
Br^-	0.14	-6.2 ± 0.9
tartrate	0.06	-1.2 ± 0.3
methanol	0.09	-1.9 ± 0.8
ethanol	0.05	-4.0 ± 1.1

The relative rate constants agree reasonably with the earlier results [4]. The observed activation energy differences, however, exhibit a trend opposite to simple expectations. The activation energies seem to differ significantly from each other, and they decrease with decreasing rate constant, i.e. the faster a reaction the higher its energy of activation.

This finding was not unique to PNDA. Some competition experiments were carried out with Safranine-T and several of the solutes listed in Table I. Although the results were unfortunately not reproducible enough for a quantitative assessment, the behaviour of the activation energies in qualitative terms was the same as that observed in the PNDA experiments.

DISCUSSION

The results show that supercooling does not exert any particular effect on competition kinetics. This agrees with the absence of any discontinuous change in the macroscopic properties of water, save for the radiation chemical yield, when it is supercooled [3]. Thus the temperature dependences of the reaction rates both below and above the equilibrium melting point can be explained on a common basis.

The unusual trend of the series of observed activation energies indicates that the rate constants do not obey the simple Arrhenius law. If the expression $k = k_o \exp(-\varepsilon/RT)$ held, a decrease in the activation energy would result in an increase in k. This is particularly true if the rates of similar reactants, like J^-, Br^- and NO_2^-, are compared where no great variation in the preexponential factor, k_o, can reasonably be expected. The difficulty cannot be removed by assuming that the PNDA+OH reaction is diffusion-controlled and obeys the Debye-equation [7]

$$k_{obs} = 4\pi\rho\, D_o\, e^{-\varepsilon_D/RT} \qquad /2/$$

where ρ is the reaction radius and ε_D the activation energy of diffusion.

Let us assume that all the reactions investigated are diffusion-controlled and their rate constants are described by the Noyes expression [8].

$$k_{obs} = \frac{4\pi\rho\ D_o \exp\left(-\frac{\varepsilon_D}{RT}\right)}{1 + \frac{4\pi\rho\ D_o \exp\left(-\frac{\varepsilon_O}{RT}\right)}{k_o \exp\left(-\frac{\varepsilon}{RT}\right)}} \qquad /3/$$

Here $k_o \exp\left(-\frac{\varepsilon}{RT}\right)$ means the rate constant which would apply if the encounter of the reaction partners were not limited by diffusion. The experimentally observed activation energy is generally defined as

$$\varepsilon_{obs} = -R \frac{d\ln k_{obs}}{d\left(\frac{1}{T}\right)} \qquad /4/$$

Introducing the expression of the diffusion-controlled rate constant into the definition of ε_{obs}, i.e. inserting eq. /3/ into eq. /4/, one finds

$$\varepsilon_{obs} = \varepsilon_D - \left(\varepsilon_D - \varepsilon\right) \frac{\exp\left(-\frac{\varepsilon_D - \varepsilon}{RT}\right)}{\frac{k_o}{4\pi\rho\ D_o} + \exp\left(-\frac{\varepsilon_D - \varepsilon}{RT}\right)} \qquad /5/$$

If $\varepsilon_D > \varepsilon$, which is most probably the case with diffusion-controlled reactions, ε_{obs} is always smaller than ε_D. Other things being equal, ε_{obs} increases with the increase of $\kappa = k_o/4\pi\rho\ D_o$. An increase of κ, however, results in an increase of k_{obs} also. Thus it is to be seen that, if eq. /3/ applies to the S+OH reactions, higher rate constants correspond to higher activation energies.

This is exactly what we have found. The data in Table I show with one single exception a simultaneous increase in k_{obs} and ε_{obs}. It should be stressed that we can explain our data only by regarding the slow reactions as diffusion-controlled ones and characterized by eq. /3/. The PNDA+OH reaction might, on the other hand, obey either eq. /2/ or eq. /3/ without causing any conflict between observation and interpretation. The Debye equation, however, is only a limiting formula of the Noyes equation for cases where diffusion is much slower than the "real" reaction. Hence if the PNDA reaction is described by the Debye equation, the faster J^- + OH reaction would obey the same law also. This would lead to the same activation energy for J^- as for PNDA. But we have found a significant difference between the two activation energies. This indicates that even the fastest of the OH radical reactions must be described by the Noyes equation.

The two problems raised in the Introduction can be answered as follows: A/ the radiation chemical kinetics of the OH radical reactions are the same in the supercooled state as in water above the equilibrium melting point; B/ all the OH radical reactions studied are diffusion-controlled, apart from the value of their rate constants, and all of them obey the Noyes equation.

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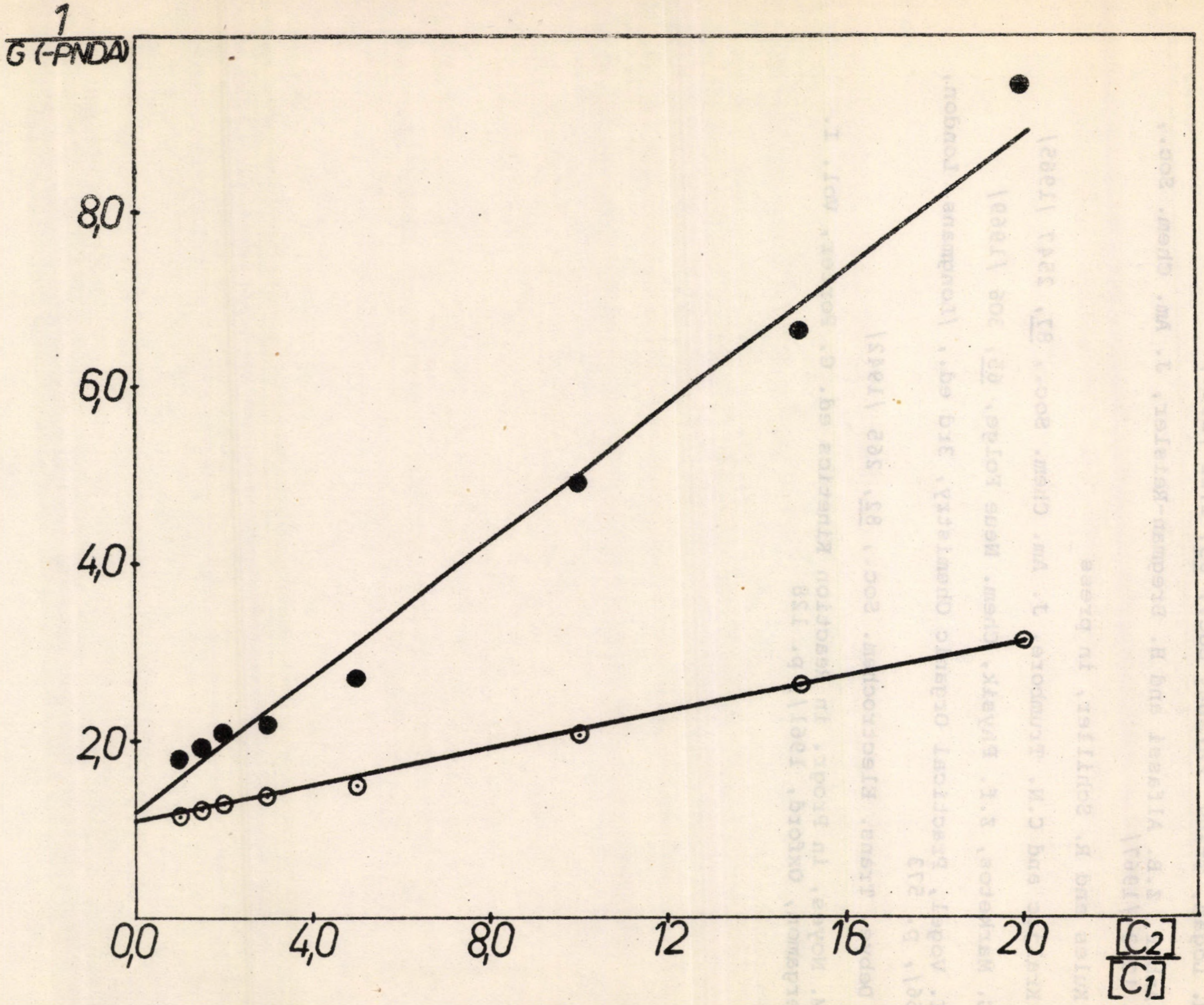

Fig. 1

The reciprocal of the yield of PNDA disappearance as a function of $[KB_r]/[PNDA]$ at two different temperatures. ⊙ 23°C, ● -8°C

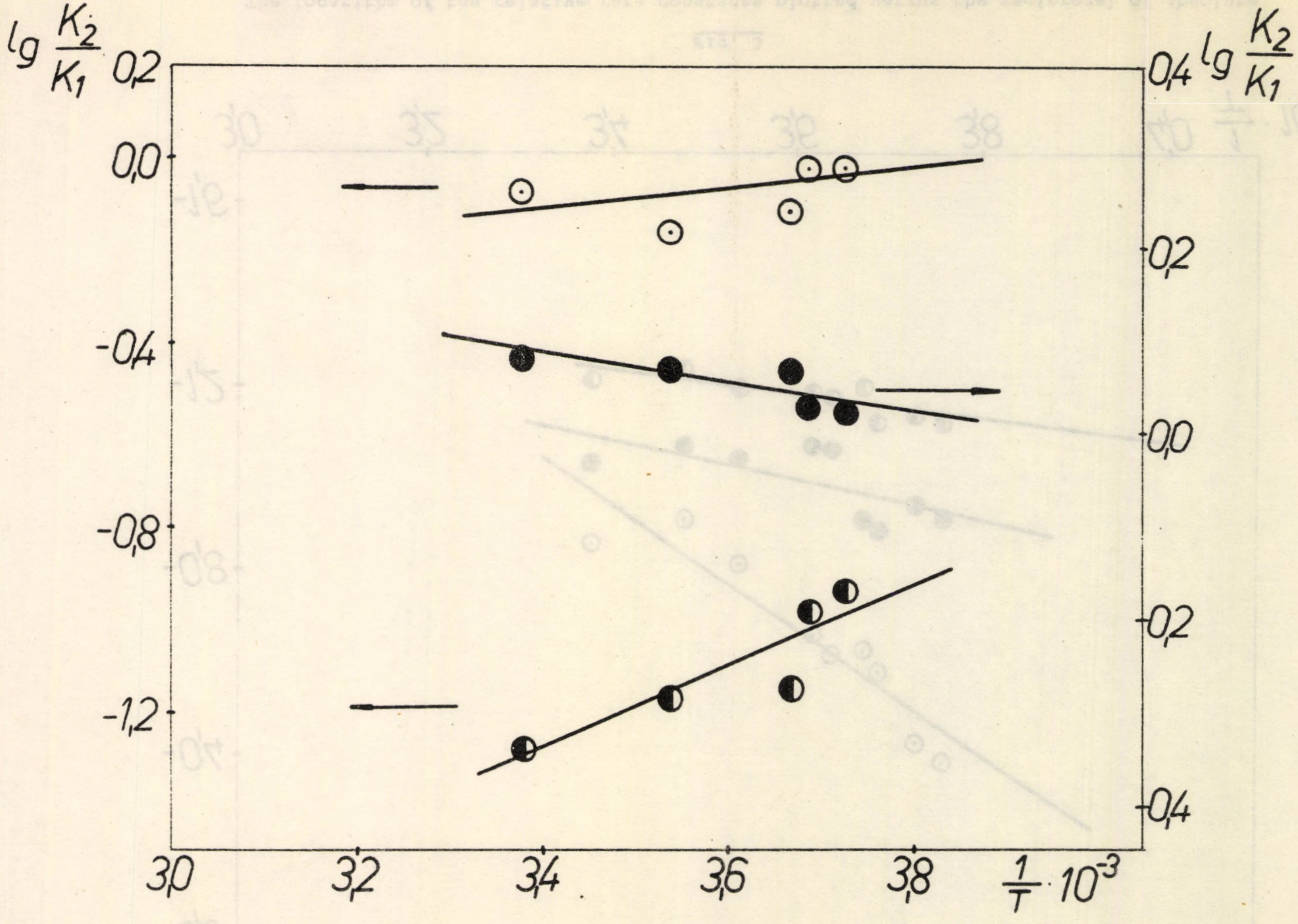

Fig. 2

The logarithm of the relative rate constants plotted versus the reciprocal of absolute temperature . ● KJ, ⊙ N_aNO_2, ◐ ethanol

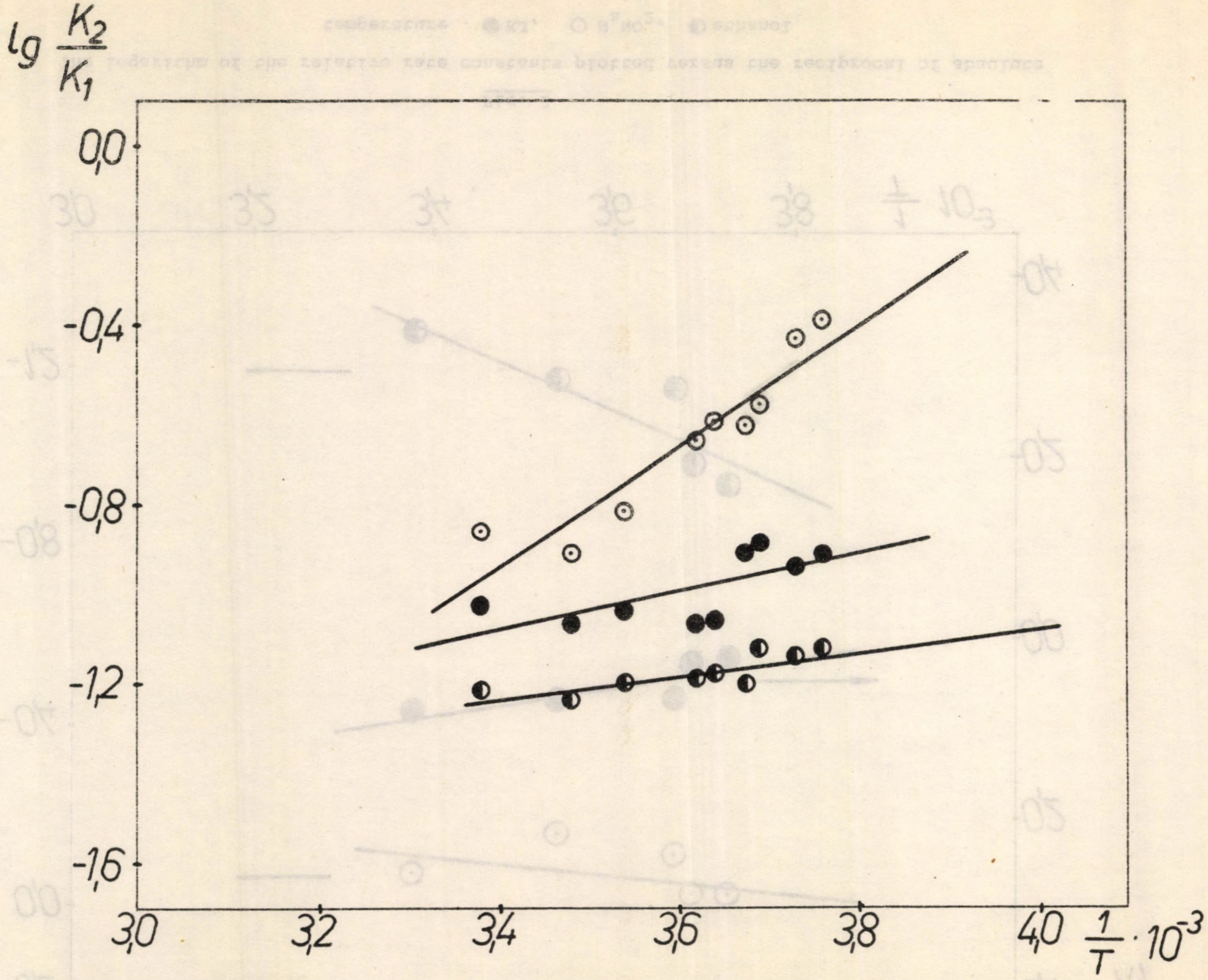

Fig. 3

The logarithm of the relative rate constants plotted versus the reciprocal of absolute temperature. ◐ tartrate, ● methanol, ⊙ KB_r

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