

REACTIVITY OF ALKYLPEROXYL RADICALS IN REACTIONS WITH  
AROMATIC NITRONS

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Interaction of tetradecylperoxyl radicals with two aromatic nitrons has been studied.

Изучено взаимодействие тетрадецилпероксильных радикалов с двумя ароматическими нитронами.

It has been established previously [1,2] that nitrons can act as "spin traps" and inhibit the oxidation of isopropylbenzene at 348 K [3]. Some aromatic carbomoyl-amidonitrons sufficiently effectively inhibit the oxidation of esters at 353-493 K [4]. We have studied the reactivity of alkylperoxyl radicals with two aromatic nitrons:  $C_6H_5CH=N(O)-C_6H_5-N-(benzylidene)-aniline-N-oxide(I)$  and  $C_6H_5NHC(O)CH=N(O)-C_6H_5-N-(2-phenylamino-2-oxoethylidene)-aniline-N-oxide(II)$ .

EXPERIMENTAL

Nitrons I and II were synthesized like in Ref. [5]. Tetradecane (TD), used as a solvent, and lauroyl peroxide (PL), used as an initiator, were purified like in Ref. [6], and by repeated crystallization from ethanol, respectively. The literature lacks data concerning rate constants of PL initiation ( $k_1$ ) in TD. Therefore, we have measured these constants at temperatures ranging within 333-363 K by the free radical acceptor method [7]. Concentration of 2,6-di-tert-butyl-4-methylphenon (ionol) used as an inhibitor, was determined by the UV spectroscopic method ( $\lambda_{max} = 280 \text{ nm}$ ,  $\lg \epsilon = 3.294 \pm 1.808$ ). Experimental values of

$k_1$  for PL in TD can be described in the Arrhenius coordinates as

$$\lg k_1 = 15.73 \pm 0.63 - \frac{135.17 \pm 4.18}{\theta} \quad (\text{s}^{-1})$$

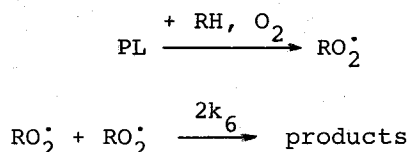
where  $\theta = 2.303 RT/1000$ ,  $R = 8.314 \text{ J/mol K}$ .

Reactivity of free radicals to nitrons I and II was determined by the kinetic spectroscopic method with measuring flow rates of nitrons in the presence of initiator and oxygen at temperatures ranging within 323–353 K. Concentration of nitrons I and II were determined at  $\lambda_{\max} = 325 \text{ nm}$  ( $\lg \epsilon = 4.372 \pm 2.929$ ), and  $\lambda_{\max} = 285 \text{ nm}$  ( $\lg \epsilon = 3.975 \pm 2.119$ ), respectively. It has been established that the optical density of products at practically complete nitron conversion is as high as 10 % of its initial value.

Stoichiometric inhibition coefficient  $\underline{f}$  for nitron II was determined from the rate of its consumption at constant initiation rate ( $V_i = 7 \times 10^{-8} \text{ mol/dm}^3 \text{ s}$ ) at concentrations ranging within  $2 \times 10^{-5} - 5 \times 10^{-3} \text{ mol/dm}^3$ . With increasing nitron concentrations, their flow rate rises and attains the limiting value  $V_\infty$ , when all peroxy radicals are completely involved into the reaction with inhibitor and the equation  $\underline{f}V_\infty = V_i$  holds. Hence we have calculated the value of  $\underline{f}$  for II:  $\underline{f} = 1.0 \pm 0.2$ . It does not depend on the temperature at  $T = 323\text{--}353 \text{ K}$ .

With concentrations of nitrons below  $1 \times 10^{-4} \text{ mol/dm}^3$ , their kinetic curves are satisfactorily transformed into straight lines in the coordinates  $\ln C_0/C-t$ , which indicates that the reaction is first order with respect to nitrons.

Pseudomonomolecular rate constant  $k_{\text{eff}}$  calculated from the above logarithmic dependence is a linear function of  $\sqrt{V_i}$  (Fig.1), which indicates that the peroxy radicals are destroyed by their interaction with each other. According to the reaction scheme



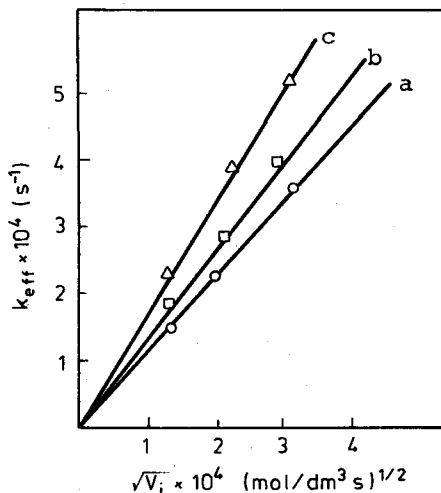
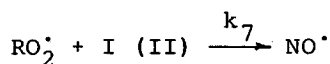


Fig. 1. Dependence of pseudomonomolecular constants  $k_{\text{eff}}$  on  $\sqrt{V_i}$  in tetradecane oxidation;  $[\text{II}]_0 = 5 \times 10^{-5} \text{ mol/dm}^3$ , a - 323 K; b - 333 K; c - 343 K

With concentrations  $[\text{II}] > 5 \times 10^{-3} \text{ mol/dm}^3$  in the initiated oxidation of tetradecane, ESR spectra exhibit a triplet signal of nitroxyl radicals, whose concentration is above  $10^{-5} \text{ mol/dm}^3$ . The nitroxyl radical formed does not affect the steady-state concentrations of  $\text{RO}_2^\cdot$  (Fig. 1).

According to the above scheme of tetradecane oxidation in the presence of nitron under steady-state conditions with respect to  $\text{RO}_2^\cdot$  concentration, the rate of nitron consumption is

$$V = k_7[\text{RO}_2^\cdot][\text{I}] = \frac{k_7}{\sqrt{2k_6}} \sqrt{V_i} [\text{I}] = k_{\text{eff}}[\text{I}]$$

The values of  $k_{\text{eff}}$  obtained from the transformation of kinetic curves, is, however, dependent on the initial concentration of nitron (Fig. 2). This can be due to the fact that in the

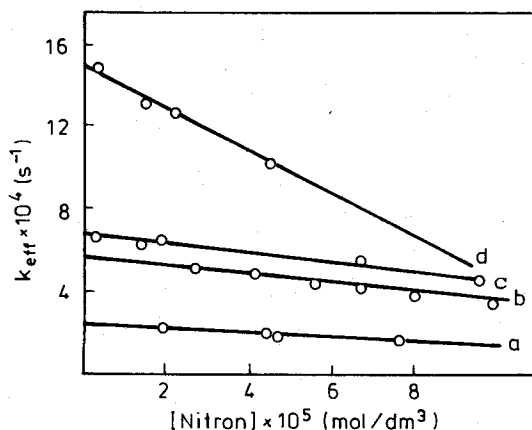


Fig. 2. Dependence of  $k_{\text{eff}}$  on the concentration of nitrons I and II at different temperatures;  $V_i = 7 \times 10^{-8}$  mol/dm<sup>3</sup> s; a - II, 323 K; b - II, 343 K; c - I, 323 K; d - I, 343 K

presence of nitron the steady-state concentration of radicals is  $[RO_2]_{\text{st}} < (V_i/2k_6)^{1/2}$ , since a certain part of radicals is destroyed with nitron molecules. Consequently,  $k_{\text{eff}}$  must depend on the nitron concentration according to the equation [8]

$$k_{\text{eff}} = \left(1 - \frac{k_7}{\sqrt{2k_6} \cdot V_i} [I]\right) \frac{k_7 \sqrt{V_i}}{\sqrt{2k_6}} = \frac{k_7 \sqrt{V_i}}{\sqrt{2k_6}} - \frac{k_7^2}{2k_6} [I]$$

Thus the extrapolation of this equation to the point, where the nitron concentration is equal to zero (Fig. 2), permits to determine the actual value of  $k_7/\sqrt{2k_6}$  (Table 1).  $k_7$  was calculated using the values of  $2k_6$  determined previously [9].

Calculation of the Arrhenius equation for  $k_7$  gives the following equations for I and II, respectively

$$\lg k_7 = 8.73 \pm 1.06 - \frac{31.17 \pm 6.88}{\theta} \quad (\text{dm}^3/\text{mol s})$$

$$\lg k_7 = 9.23 \pm 0.82 - \frac{37.16 \pm 5.29}{\theta} \quad (\text{dm}^3/\text{mol s})$$

where  $\theta = 2.303 RT/1000$ ,  $R = 8.314 \text{ J/mol K}$ .

Table 1  
Value of  $k_7/\sqrt{2k_6}$  and  $k_7$  for nitrons I and II at different temperatures

T (K)	I		II	
	$k_7/\sqrt{2k_6}$ ( $\text{dm}^{3/2}/\text{mol}^{1/2}$ $\text{s}^{1/2}$ )	$k_7 \times 10^{-3}$ ( $\text{dm}^3/\text{mol s}$ )	$k_7/\sqrt{2k_6}$ ( $\text{dm}^{3/2}/\text{mol}^{1/2}$ $\text{s}^{1/2}$ )	$k_7 \times 10^{-3}$ ( $\text{dm}^3/\text{mol s}$ )
323	2.51±0.04	4.36±0.73	0.89±0.02	1.55±0.03
333	4.16±0.11	7.75±0.21	1.48±0.02	2.75±0.03
343	5.63±0.15	10.70±0.29	2.18±0.03	4.15±0.05
353	5.82±0.04	11.60±0.08	2.48±0.04	4.95±0.08

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