Investigation of the reaction of peroxide radicals derived from di-*n*-butyl ether with *p*-phenylenediamine by kinetic spectrophotometry

*N. V. Zolotova** *and V. V. Kharitonov*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 515 3588

The kinetics of consumption of *p*-phenylenediamine (PDA) in di-*n*-butyl ether (BE) subjected to oxidation was measured by following the accumulation of the product of the transformation of PDA. The effective rate constant of the reaction of peroxide radicals derived from BE ($RO_2^{\cdot}$) with PDA was measured ($k_7 = 2 \cdot 10^4$ L mol^{-1} s^{-1}) by the inhibitor method. Evidence confirming the formation of a stable complex of $RO_2^{\cdot}$ with PDA were obtained. This leads to retardation of oxidation without the formation of hydroperoxides of BE (ROOH) in the acts of chain termination on PDA.

Key words: inhibitor, inhibitor method, rate constant, di-*n*-butyl ether, *p*-phenylenediamine.

The mechanism of action and the efficiency of an inhibitor (A) depend on the structures of both A itself and of the substrate to be oxidized. The action of A in paraffins and aromatic hydrocarbons has been studied in the most detail. Data on the peculiarities of oxidation and the mechanism of action of A in oxidizable oxygen-containing compounds are much more scarce. We have previously[1,2] studied the initiated oxidation of di-*n*-butyl ether (BE) in the presence of aromatic amines and sterically hindered phenols as inhibitors. Among them, *p*-phenylenediamine (PDA), which retards the oxidation of BE without the formation of hydroperoxides,[2] turned out to be the most interesting. The purpose of the present work was to measure the rate constant of the reaction of peroxide radicals derived from BE with PDA (k_7).

Experimental

Di-*n*-butyl ether (pure grade) was treated with a saturated solution of $KMnO_4$ containing 5% NaOH. Then it was washed with water, a saturated solution of $Na_2S_2O_3$, and water again, and dried with Na_2SO_4. The purified BE was distilled in the vacuum of a water-jet pump at 35 °C. The content of hydroperoxides in the distilled BE was equal to $\sim 1 \cdot 10^{-4}$ mol L^{-1}.

Azobisisobutyronitrile used as an initiator (I) was recrystallized from ethanol. The rate constant of decomposition of I into radicals (k_i) in BE at 60 °C is equal[1] to $0.7 \cdot 10^{-5}$ s^{-1}. *p*-Phenylenediamine was purified by sublimation *in vacuo*. Spectral analysis was carried out on a Specord UV-VIS spectrophotometer.

Results and Discussion

At sufficiently high concentrations, PDA retards the oxidation of BE so strongly that the measurement of the very low rates of oxygen consumption becomes insufficiently reliable for determining the numerical value of k_7. Therefore, we used another known procedure,[3] according to which the k_7 value is determined from the kinetics of consumption of the inhibitor. It is noticed that when BE is oxidized in the presence of PDA, the optical density (*D*) of the solution increases in the course of the reaction. The interval during which *D* increases is equal to the period of retardation of the oxidation, which was determined from both the kinetics of the consumption of oxygen and the accumulation of ROOH.[2] The formation of ROOH begins only after PDA has been consumed and *D* has reached a constant value. It can be assumed that in BE, which undergoes oxidation, PDA is transformed quantitatively into a colored product. It is reasonable to compare PDA with *N,N'*-di-β-naphthyl-*p*-phenylenediamine (NPA), the kinetics of consumption of which in similar experiments is determined by the kinetics of the accumulation of quinoneimine, which is the sole product of the transformation of NPA under these conditions.[4] In our case, for quantitative measurements, the extinction coefficient (ε) of the product of the transformation of PDA was determined at 400 nm, where the initial PDA does not absorb: ε_{400} = 1450 L mol^{-1} s^{-1}.

To check the validity of the assumption that the kinetics of the accumulation of the product can be

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2902—2903, December, 1996.

1066-5285/96/4512-2753 $15.00

identified with the kinetics of the consumption of A, we compared the measured rates of formation of the products with the specified initiation rates (k_i[I]). It turned out that the rate of accumulation of the product at sufficiently large [A] is equal to $1/2 \times k_i[I]$ in accordance with $f = 2$, which has been determined previously in the experiments on the consumption of oxygen and the accumulation of ROOH.[1,2] Therefore, under the conditions of our experiments, the kinetics of the consumption of A can be determined from the kinetics of the accumulation of the product of the transformation of PDA.

According to the known procedure,[3] the kinetics of the consumption of A when $k_7[A] \ll k_6[RO_2^{\cdot}]$ allows us to determine k_7 from the formula

$$k_7 = \frac{\log\dfrac{D_\infty - D_0}{D_\infty - D_t}\cdot\sqrt{2k_6}}{0.43\sqrt{k_i[I]}\cdot t}, \qquad (1)$$

where D is the optical density of the solution when the time of the experiment t is 0 and ∞. Using the $2k_6$ value for BE obtained previously[5] ($2k_6 = 1.4 \cdot 10^8$ L mol^{-1} s^{-1}), we obtain $k_7 = 2 \cdot 10^4$ L mol^{-1} s^{-1} (Fig. 1).

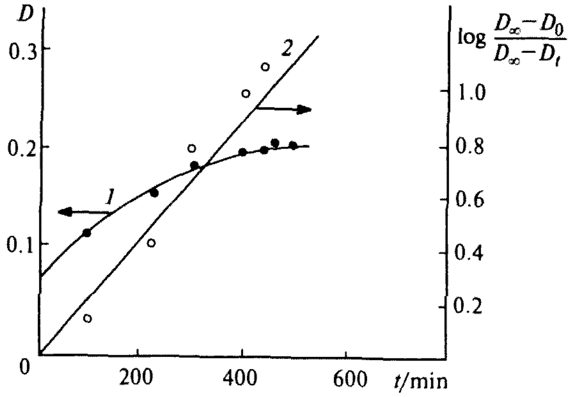

Fig. 1. Kinetics of changes in D at 400 nm (a 5-cm cell) for the initiated oxidation of BE in the presence of $2.5 \cdot 10^{-5}$ mol L^{-1} PDA at 60 °C (initiation rate $1.88 \cdot 10^{-9}$ mol L^{-1} s^{-1}) (*1*); *2*, the same in coordinates of Eq. (1).

As has been found,[6,7] the efficiency of A in oxygen-containing compounds is substantially lower than in nonpolar hydrocarbons due to complex formation between A and the substrate. In our case, these complexes can also form through hydrogen bonds between the >NH groups of A and the oxygen atoms of BE. Therefore, the k_7 value determined by us is the effective constant. When the determined[7] value of the equilibrium constant of formation of this complex is used, the true k_7 value increases 5—10 times. Under conditions of the initiated oxidation of BE, the reaction of PDA with $RO_2^{\cdot}$ plays a decisive role, and other possible routes of consumption of A can be neglected.[1] We believe that the main specific feature of the reaction of PDA with $RO_2^{\cdot}$ is that it occurs *via* a mechanism[8] that involves $RO_2^{\cdot}$ "sticking" to PDA to form a complex, whose reaction with a second $RO_2^{\cdot}$ radical results in chain termination. The formation of this complex is favored by the fact that the oxidation of different substrates results in the formation of products of the transformation of PDA with different ε. For example, in BE ε_{400} is equal to 1450 L mol^{-1} cm^{-1}, this value is equal to ~800 in toluene and cumene, while in heptane and benzene it is ~350 L mol^{-1} cm^{-1}. In the case of an inhibitor that "works" according to the "classical" mechanism (with abstraction of a hydrogen atom), the ε value of the product of the transformation of A should not depend on the substrate whose oxidation is retarded by A.

Thus, the effective rate constant of the reaction of peroxide radicals derived from BE with PDA ($k_7 = 10^4$ L mol^{-1} s^{-1}) was determined by kinetic spectrophotometry from the kinetics of the accumulation of the product of the transformation of PDA.

References

1. N. V. Zolotova and V. V. Kharitonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1904 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1705 (Engl. Transl.)].
2. N. V. Zolotova and V. V. Kharitonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1268 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1139 (Engl. Transl.)].
3. E. T. Denisov and A. L. Aleksandrov, *Zh. Fiz. Khim.*, 1965, **72**, 491 [*Russ. J. Phys. Chem.*, 1965, **72** (Engl. Transl.)].
4. L. N. Denisova, E. T. Denisov, and D. I. Metelitsa, *Zh. Fiz. Khim.*, 1970, **77**, 1670 [*Russ. J. Phys. Chem.*, 1970, **77** (Engl. Transl.)].
5. J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 1970, **48**, 873.
6. G. A. Kovtun and A. L. Aleksandrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1946 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22** (Engl. Transl.)].
7. R. L. Vardanyan, *D. Sci.* (*Chem.*) *Thesis*, OIKhF AN SSSR, Chernogolovka, 1986, 313 pp. (in Russian).
8. C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, 1954, **76**, 3861.

Received December 15, 1995;
in revised form April 11, 1996