Introduction The ozonolysis of oxygen-containing compounds is a promising process that takes place under mild conditions and yields compounds of a higher oxidation state than that of the starting compounds. It may find various applications in chemical and pharmaceuticals industries, fine organic synthesis, etc. (1-2). The widest application, in this respect, has been found for the oxidation of primary and secondary alcohols respectively into their corresponding aldehydes and ketones. For example in the cases of the oxidation of open-chain (simple) and cyclic secondary alcohols the yield of ketones is within the range 57% up to 83% (3). Moreover, the considered interactions are extremely important from an ecological point of view for the utilization and purification of industrial wastewaters, originating from hydroxybenzene production, through their partial or complete oxidation (4-24). The importance of this process for theory and practice gave us an impetus to carry out systematic investigations (25-35). The aim of the present paper is the precise determination of the rate constants of ozonolysis of some more widely occurring representatives of the studied classes of organic compounds. Applying the activated complex method (ACT) (36) and collision theory (CT) (36) some theoretical investigations have also been carried out elucidating the structure of the transition state formed in the course of the reaction. On the basis of the correlation between the results from the experimental and theoretical studies some peculiarities in the mechanism of ozone reactions with the considered classes of oxygen containing compounds have been established. Experimental Ozone has been obtained from dry oxygen by means of a silent discharge of 5-8 kV at an oxygen flow rate of 0.1 L/min. The ozone concentration, 10-5 -10-3 M, has been measured spectrophotometrically in the wavelength region of 254-300 nm in a 5 cm quartz gas cell. Methods The UV, IR, ESR spectra were registered on standard equipments, as well as HPLC, and GC analyses. Kinetic Measurements Static Method Pure reagent or reagent solution was injected into thermostatic 1 cm quartz cuvette, containing a solution of ozone in CCl4, the time of mixing being less than 0.2 second. Ozone concentration was monitored spectro-photometrically in the region of 270-290 nm. At [RH]o/[O3]lo>100, the ozone pseudomonomolecular constant k`=k[RH]o was determined on the basis of the equation lg([O3]lo/[O3]lt)=k`t where [O3]lo and [O3]lt are the initial and current concentrations of ozone in solution, respectively (27). Dynamic Method The ozone was bubbled through a cylindrical glass reactor with inner diameter Æ=1.7-3.7 cm and height 7-15 cm, supplied with porous glass grit-G2 at its bottom. The accuracy of maintaining constant temperature was ±0.1oC. Conventionally, gas flow rate was v=0.1 L/min; the solutions volume was V=10 ml; the ozone concentrations at the reactor inlet ([O3]o) varied from 10-6 to 10-3 M; the solvent was CCl4; [RH]o=10-4-101 M. The inlet and outlet ozone concentrations were measured in the gas phase in the 254-300 nm wavelength range. The determination of rate constants is based on the approach, which connects the balance of consumed ozone with the rate of the chemical reaction - Eq. (1): w([O3]o-[O3]g) = k[O3]l[RH] (1) where w is the relative flow rate of ozone–oxygen gas mixture (in litres per L of solution per sec); [O3]o and [O3]g are the ozone concentrations at the reactor inlet and outlet, respectively, [O3]l is ozone concentration in the solution; [RH] is concentration of the reagent. This model is valid in all cases, when the rate of ozone absorption is considerably greater than the rate of the chemical reactions. If in the case of a bimolecular reaction, in accordance with Henry’s Law, [O3]l is substituted with a[O3]g, where a is Henry’s coefficient, Eq. (1) can be transformed into Eq. (2) (1): k = w.D[O3]/([RH]. a[O3]g) (2) One of the widely applied criteria with respect to the conditions of validity (applicability) of Henry’s Law is the expression: DO3.k1¢/kL21 where DO3 is the diffusion coefficient of ozone in the solution; kL=DO3/d is the coefficient of mass transfer in the liquid phase, and d is thickness of the boundary layer in the hydrodynamic model of renovation surface; or kL=(DO3.s)1/2, where s is the time interval of renovation. In the case of applying the bubbling method with small bubbles (diameters up to 2.5-3 mm) then kL=0.31x(gn)1/3x(DO3/n)2/3, where n=h/r, is the kinematic viscosity of the solvent, h is the viscosity of the solvent, r is the solvent density, g is the earth acceleration. Usually the kL values are of the order of 0.1-0.05 cm/s. As k1`=k[RH]o in most of the cases it is possible to select such values for [RH]o, at which the criterion for applicability of Henry’s Law is fulfilled (34). In order to minimize the influence of the so-called “effect of delay in the response function”– [O3]g=f(t) upon calculating the values of k such sections of the kinetic curves are selected, which appear to be practically parallel or only slightly inclined with respect to the abscissa: k1`a[O3]g>> d[O3]g/dt. The advantages and limitations of this method have been discussed in detail in (37, 38). Despite some contradictory observations, the significant part of rate constants of ozone with organic compounds and polymers are obtained on the basis of Eq. (2) (1, 34). Results and their discussion Ethers Reactions of ozone with alcohols and ketones were considered in the previous parts of the review (39-40). Investigations of ozone reactions with ethers began as early as the last century (41-45). Results of these studies are summarized and reported by Bailley in his review (45). The main products formed during ozonolysis of aliphatic ethers are alcohols, aldehydes, esters, acids, hydrotrioxides (HTO), hydrogen and organic peroxides, singlet oxygen and water. Price and co-workers (47) proposed the so-called ‘insertion’ mechanism, according to which ozone is inserted into the a-C-H bonds at the first step through a 1,3-dipolar addition, thus forming unstable HTO. This mechanism was also supported by the data of Erickson and Bailey (45, 46, 48) and Murray and co-workers (49), who measured the activation parameters of the decomposition of a series of HTO, obtained by the ozonolysis of some ethers. Giamalva and co-workers (50) summarized the possible mechanisms known today, i.e., interaction with the ether oxygen atom, 1,3-dipolar insertion of ozone into the a-C-H bonds, homolytic abstraction of the a-H atom and heterolytic abstraction with carboanion and carbocation formation. These authors clearly indicate the predominance of the one-step mechanisms with transfer of a hydrogen atom, hydride anion or cation. As it was mentioned above, the low-temperature ozonolysis of ethers yields HTO, which however are stable at very low temperatures. At normal temperatures the composition of the products is found to be different from that after the decomposition of HTO. These two reasons gave us impetus to carry out extended studies on the ozone reaction with ethers in order to establish the real mechanism of these reactions at normal temperatures. It was estimated, based on kinetic curve of ozone consumption (Figure 1) and eq. (2), that the kinetic constant of the ozonation of diethyl ether (DEE) at t = -5°C is 0.9 M-1.s-1. Taking into account the area, comprised between the straight line y=[O3]o and the kinetic curves of DEE, which have been obtained at the lower concentrations of the reactant, the amount of ozone, consumed in the reaction has been determined. Juxtaposing this amount with the initial quantity of DEE in the reactor the stoichiometric coefficient of DEE ozonolysis has been estimated to be 1. Figure 1 - Kinetic curve of ozone concentration at the reactor outlet: 10 ml, 92 mM DEE, at -5oC The calculated stoichiometric coefficient of the ozonation reaction with other ethers was also unity. The kinetics of ozonolysis was studied with the example of n-dibutylether (DBE). The kinetic curves of the reaction product formation and the initial ether consumption are shown in Figure 2. The following products were identified by gas chromatography-mass spectrometry in the reaction mixture after 10 minutes (mass spectra of the obtained compounds are given below): 130 * 57 41 87 56 55 101 39 130 43 45 * n-Dibutylether, 74 * 56 41 43 42 55 39 57 45 40 41 * n-Butanol, 72 * 44 43 41 72 57 42 38 37 40 71 * Butanal, 88 * 60 73 41 42 43 45 39 55 61 88 * Butiryc acid; 144 * 71 89 56 43 41 57 60 73 55 42 * Butyl butyrate and 164 *& 247 * - Chloro-containing compounds like: CH3(CH2)2CH(Cl)O(CH2)3CH3 (Mw 164.4) and CH3(CH2)2CH(CCl3)O(CH2)3CH3 (Mw 247). Figure 2 - Kinetics of product formation and consumption of DBE during ozonolysis at ambient temperature, [O3]o = 2.34 × 10-4 M Figure 3 - Dependence of the reaction rate of DBE ozonation (21oC) on the concentration of ozone (1) at [DBE] = 10 mM and DBE (2) at [O3] = 0.1 mM The rate of DBE decomposition (7.4×10-5 M.s-1 determined on the basis of Figure 2) is almost equal to the sum of butanal (6.5×10-5 M.s-1), butanol (6.71×10-5 M.s-1) and butyl butyrate (1.0×10-5 M.s-1) formation rates. The kinetic curves of butanol and butanal formation have almost the same slope and they start without any induction period. This could mean that they are formed in parallel reactions from a common precursor. The rate of butylbutyrate accumulation, as it is demonstrated by its kinetic curve, is approximately 7 times lower. The latter indicates that their formation is occurring in a parallel reaction to butanol (butanal) formation, most probably from the same precursor. The ratio of product amount to initial DBE amount after 10 minutes was found to be 1:1. This means that the share of the auto-oxidation process is negligibly small, although we have identified some butyric acid by its IR spectrum (1765 cm-1 (monomer) and e = 1470 M-1.cm-1) resulting from the butanal oxidation. The possible existence of a common precursor raises the question about its nature. Such a precursor could be either a-hydroxyether (EOH) or a-hydrotrioxyether (EOOOH), which can produce further through intermolecular disproportionation simultaneously aldehyde and alcohol: Probably, the intermolecular reaction of EOOOH disproportionation is preferable, because of the six-member-ring transition state, while EOH disproportionation occurs via a strained four-member-ring transition state, which is energetically unfavorable. If EOH is assumed to be the precursor, then the butylbutyrate should be a major reaction product as a result of the rapid oxidation of EOH by ozone: (3) which has not been observed experimentally. When EOH is assumed to be the precursor, it is difficult to imagine its one-step transformation into an ester without any additional assumptions. Also the solvent, CCl4, could not affect at all this transformation, bearing in mind its weak oxidizing properties and its non-specificity. The formation of the ester from EOOOH in a single step can be easily presented through a four-member-ring transition state: (3’) The formation of four-member transition state will be more unfavourable than the six-member transition state. This conclusion is in agreement with the kinetic data, namely, the rate of ester formation is approximately 7 times lower than that of alcohol and aldehyde formation. Direct evidence for EOOOH formation was found only after prolonged ozonation for 24 h at -78°C (51-54). The NMR spectrum of the oxidate has a signal at d=13.52 ppm, which is attributed to OOOH. Figure 3 represents the dependences of the rate of ozonation of DBE on the concentrations of the ozone and that of DBE. Judging from the linear character of the dependences, in conformity with equation 2, it follows that the order of the reaction is unity with respect to each one of the two reactants and therefore rate law can be written in the form W = k×[DBE][O3]. Based on the results discussed above, a scheme of the ozone reaction with aliphatic ethers is proposed in Scheme 1. Ether + O3 ® EOOOH (k1) EOOOH ® Alcohol + Aldehyde + O2 (k2) EOOOH ® Ester + H2O2 (k3) Scheme 1 The formation of chlorine-containing compounds (1-2%) can be explained by the presence of radical intermediates in the reaction mixture. This means that EOOOH will also be decomposed via radical route: EOOOH ® EO· + ·O2H (k4) EO· + EH ® EOH + E· (k5) E· + O2 ® EO2· (kp’) E· + CCl4 ® ECl + CCl3· (kp’) EO2· + EH ® EOOH + E· (kp) E· + CCl3· ® ECCl3 (kt’) 2EO2· ® non-radical products (kt) The validity of the mechanism, indicated above, was confirmed by the good agreement between the experimental points on the DBE decomposition curve and the product accumulation and by the theoretical curves, calculated according to the scheme and given in Figure 2. For example, the curve describing the DBE consumption is obtained from Equation 4: [DBE]t = [DBE]0.exp(-k’t) (4) where k' is the constant, measured by the stop-flow method - 1.26×10-3 s-1, while the corresponding bimolecular constant is 6.3 M-1.s-1. A comparison of the experimental values and calculated estimates of A, assuming linear (LC) and cyclic (CC) forms of the activated complex (AC) has been made. The kinetic constants of ozone reaction with diethylether (EtE), dichlorodiethylether (DClEtE), di-iso-propylether (i-PrE), di-n-butylether (n-ButE), di-iso-amylether (i-AmE) and di-n-amylether (n-AmE) in CCl4 are given in Table 1. Table 1 - Rate constants of ethers ozonations at various temperatures (oC) Ether -15oC -6oC -5oC 3.5oC 4oC 10oC 13oC 21oC 24oC EtE 0.5 0.9 1.0 1.2 1.6 2.2 2.4 3.1/ 3.0 3.6

DClEtE - - 0.009 0.016 - - 0.028 0.035/ 0.04 - i-PrE - - 1.6 1.9 - - 3.4 5.4/ 5.1 - n-ButE - - 1.9 2.1 - - 4.3 6.3/ 6.3 - i-AmE - - 1.9 2.5 - - 4.1 7.8/ 7.0 - n-AmE - - 2.2 2.8 - - 4.2 7.8/ 7.5 - Note: In column 9, after the slash the values of the constants determined by stop-flow method are given. The rate constants for EtE, n-ButE, i-AmE and n-AmE have similar values. All these ethers have close a-C-H bond energies and similar electronic environment. The value of the rate constant for i-PrE ozonation is also close to those mentioned above, while the constant for DCIEtE has 100 times lower value. In DIPE the presence of tert-C-H bonds, should contribute to their higher reactivity because of the lower energy of these bonds (55). The presence of oxygen, however, and the more difficult stabilization of the transition state due to steric factors, makes this interaction slower. The very low rate constant of DClEtE ozonation can be attributed to the strong electron-accepting properties of the chlorine atom. Arrhenius parameters, calculated on the basis of the data in Table 1, are summarized in Table 2. The comparison of the results, obtained with reference data, shows a good coincidence in regard to the values of the rate constants at 21°C. Only a slight difference in the activation energies was observed. Perhaps, it is the heat of ozone dissolution in CCl4 that needs to be taken into account as the reason for these differences. All reaction schemes, found in the current literature, describe the ozonation of ethers proceeding through two geometric forms of the activated complex - LC and CC: The CC has a more compact structure, without any possibility for free rotation. It can be a transition state for the following reaction: Table 2 - Arrhenius parameters of ozone reaction with some aliphatic ethers Ether k, M-1.s-1 lg A Ea, kcal/mol EtE 3.1 6.4 (7.3) 7.9 (9.9) DClEtE 0.035 4.9 (5.5) 8.5 (10.1) i-PrE 5.4 6.3 (7.9) 7.6 (10.0) n-ButE 6.3 (6.0) 6.6 (7.4) 7.8 (9.7) i-AmE 6.8 6.6 7.8 n-AmE 7.8 6.5 7.6 THydP (1.3) (6.8) (9.7) THydF (12.3) (6.6) (8.2) Note: The values in brackets are taken from reference (56); THydP and THydF are tetrahydropyrane and tetrahydrofurane, respectively. Table 3 - Heats of formation (DH) in kcal of initial, intermediate and final products, van der Waals radii of the ethers and free rotation energy (Efr) around H-O bond Ether r, [Å] DH, EH DH, EOOOH DH, E· DH, E+ Ea, kcal/mol EtE 3.18 -68 -66 -32 135 1.3 dClEtE 3.51 -74 -73 -41 132 2.2 i-PrE 3.48 -76 -74 -42 125 1.4 n-ButE 4.03 -81 -79 -47 120 1.3 i-AmE 4.31 -87 -86 -53 115 1.3 n-AmE 4.45 -86 -85 -51 116 1.3 EH + O3 ® EOOOH ® products (a) where EOOOH is being formed in one step via 1,3-dipolar insertion. The LC structure is an open one, allowing free rotation around H-O and O-O bonds. LC can be a transition state for the reactions: EH + O3 ® E· + HO3· ® EOOOH ® products (b) EH + O3 ® E+ + HO3- ® EOOOH ® products (c), in which an H atom or hydride anion abstraction occurs and EOOOH is formed during the second step. The necessary parameters for estimating the A values are represented in Table 3. The calculated values of A are shown in Table 4. The good agreement between the calculated estimates and experimental values for A confirms the conclusion that the geometry of the transition state is a linear (LC) and abstraction mechanisms (a) and (c) seem more probable. Table 4 - The calculated pre-exponents (A) and steric factors (p) Ether lg A, CT lg A, CC lg A, LC p×106, CC p×106, LC AcalcLC/ Aexp EtE 11.66 4.02 6.40 0.02 5.5 1 dClEtE 11.66 3.62 4.99 0.009 0.2 1.23 i-PrE 11.67 4.28 6.35 0.04 4.8 0.91 n-ButE 11.72 3.99 6.09 0.02 2.3 0.31 i-AmE 11.75 3.90 6.00 0.01 1.8 0.25 n-AmE 11.74 3.77 5.87 0.01 1.3 0.23 Note: the values of A in columns 3 and 4 are per one equivalent a-C-H atom. In order to evaluate which one of the mechanisms is occurring we used the thermodynamic parameters shown in Table 3. The calculated heats of formation of the individual compounds fit well to the experimentally measured values (57, 58). Using different expressions for the Hamiltonians, we have obtained the following values for DH: O3 -33.3 kcal against the literature data of (34.1); HOOOH -17.8 (-17.1); HOOO -9.2 (-17.8); HOOO -20.3(-24.9); HO -5.2(-25.8). DH = –DH (EH) – DH (O3) + DH (EOOOH) (a) DH = –DH (EH) – DH (O3) + DH (E·) + DH (HO3·) (b) DH = –DH (EH) – DH (O3) + DH (Å+) + DH (HO3-) – e2/rip – Es (c) where both types of values: 1) for energy of interaction between two charged particles (e2/rip = 5.4 eV = 2.06x10-16 kcal), and 2) for energy of solubility in tetrachloromethane solution (Es = 17 kcal) were taken from reference (59). The calculated values for DH are depicted in Table 5. Table 5 - Calculated heats of investigated reactions according to mechanisms a, b and c Ether a, kcal/mol b, kcal/mol c, kcal/mol EtE -32 -16 0 dClEtE -33 -19 6 i-PrE -32 -18 1 n-ButE -32 -18 1 i-AmE -32 -18 2 n-AmE -33 -17 2 From thermodynamic point of view, (a) is the preferable mechanism and out of (b) and (c), (b) is more plausible