

Reaction of CH_3O_2 Radicals with Acetaldehyde on the TiO_2 Surface

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In atmosphere enter significant amount of organic pollutions, including methane, acetaldehyde and etc. During the gas phase chemical conversion of these substances in the presence of solid surface the remarkable role in the process play the heterogeneous radical stages. The similar reactions on a surface of the NaCl , KCl , TiO_2 included in natural atmospheric aerosols can apparently influence on the composition of troposphere and on the combustion and oxidation processes.

Background

ESR measurements of the heterogeneous interaction of CH_3O_2 radicals with an organic compound (methane) depending on its initial concentration on the surfaces of NaCl , KCl , TiO_2 has shown [1-3], that in contrast with salt surface, on the surface of titanium oxide the dependence of radicals concentration on the initial concentration of organic reagent has complex character. On titanium oxide surface under some conditions not only the decrease, but the remarkable increase of radicals concentration has been discovered. The observable rise of peroxy radicals quantity in comparison with their initial quantity is attributed to the additional heterogeneous radical consumption of organic compound initiated by the researched reaction.

Aim of the work

Present study is carried out for establishing the general character of discovered phenomenon of radicals multiplication and the influence of the nature of organic compound on the kinetic peculiarities of studied process.

Experimental conditions

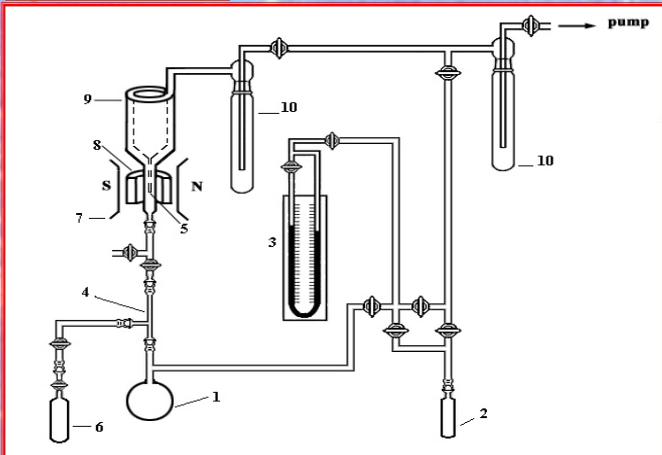


Fig.1. Scheme of major units of set-up

1- quartz vessel for the adsorption of peracid, 2- vessel with peracid, 3- manometer, 4- reactor, 5- freezing unit, 6- vessel with reagent (CH_4), 7- magnet, 8- resonator of the ESR spectrometer, 9- quartz Dewar, 10- traps

Experiments were carry out using radicals frizind method combining with ESR spectroscopy. Reactions of RO_2 radicals with reagents were studied at pressures of the order of 10^{-2} torr. The dimension and construction of the reactor (capillary tube $l = 2\text{cm}$, $d = 0.15\text{cm}$) as well as the low pressure used in experiments excluded significant homogeneous interaction of reagents. The residence time (τ) of reacting mixtures in the capillary reactor takes much less time, than that of the homogeneous interaction of CH_3O_2 radicals with reactants (τ_1). The absence of the interaction of peroxy radicals with reagents in the apparatus beyond the capillary reactor was established by rate calculations and special experiments, that introduced reagents directly into this zone. The consumption of radicals in the post capillary reactor zone was not observed. The oxide surfaces were created by treating reactor with 10% suspension of TiO_2 . The generation of RO_2 radicals into gas phase was carried out by heating the adsorbed peracetic acid [2]. Early was shown, on solid surface the heterogeneous recombination of CH_3CO_3 radicals was not detected for temperatures up to 373K. In experiments, the significant heterogeneous reaction at temperatures up to 353K, even by doubling the surface area of the reactor, has not been detected. In addition a quadratic dependence of radical loss on radical concentration has not been observed. Therefore in the presence of reactant the radical uptake can be attributed generally to the reaction with reactants. The interaction of radicals with various reactants was quantified by measuring the consumption of RO_2 radicals in relation to their initial quantity.

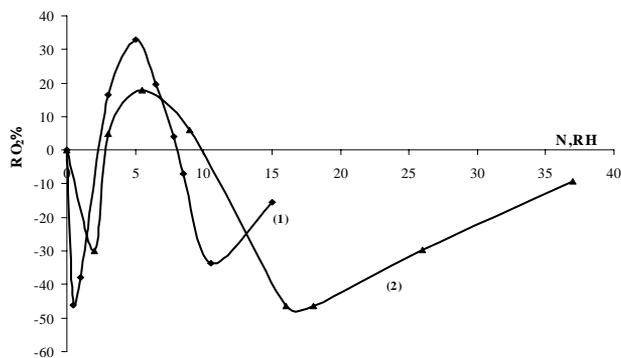


Fig.2. Dependence of the change in the amount of radicals ($\Delta \text{RO}_2, \%$) on the initial amount of acetaldehyde (curve 1) and methane (curve 2), ($N \times 1.6 \times 10^{16}$ molecules) at 293 K, $[\text{CH}_3\text{O}_2]_0 = 25$ arbitrary units.

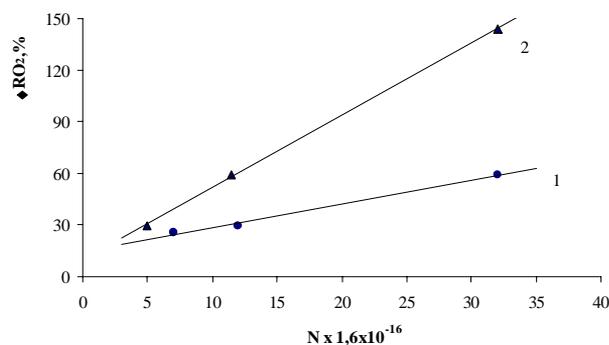


Fig.3. Dependence of CH_3O_2 radicals increasing ($\Delta \text{RO}_2, \%$) on the initial quantity of CH_4 ($N \times 1.6 \times 10^{16}$ molecules). 1- $T=293\text{ K}$, 2- $T=353\text{ K}$. The TiO_2 covering is thick.

Results and discussion

Two curves on Fig.1 indicate the similar complex character of the reaction in the case of different organic compound. The observation of radicals multiplication not only in the case of hydrocarbon but in the case of aldehyde can serve as the indication of the general character of the discovered phenomenon [3]. As regards to the quantitative picture there is the significant difference due to the better acetaldehyde adsorption and the higher rate constant of the heterogeneous consumption of acetaldehyde than methane. Hence the rate of the initiation of the chain consumption of molecular organic reagent is higher. Therefore in the case of acetaldehyde the higher degree of radicals multiplication is observed. The additional consumption of organic compound is attributed to chain mechanism initiated by the radical decay of ROOH , forming during the interaction of peroxy radicals with organic compound. The value of radicals rise apparently depend on number of active centers on the surface of reaction vessel. Therefore, with the increase of TiO_2 concentration on reactor walls the absolute value of radicals for a same quantities of organic compound increase too (Fig.3).

Modeling [4] the interaction of CH_3O_2 radicals with organic compound (methane, aldehyde) in the presence of oxygen traces on the oxygen containing surfaces (VALKIN computer program, Langmuir-Hinshelwood approach) confirmed the explanation of the observed kinetic peculiarities by the chain radical mechanism.

Conclusion

The important conclusion is that the interaction of peroxy radicals with different organic compound on the oxygen containing solid surface in certain conditions can take place with the multiplication of radicals because of initiation of chain consumption of molecular reagent.

Referece

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