Comparison of reaction rates for ozone—alkene and ozone—alkane systems in the gas phase and in solution

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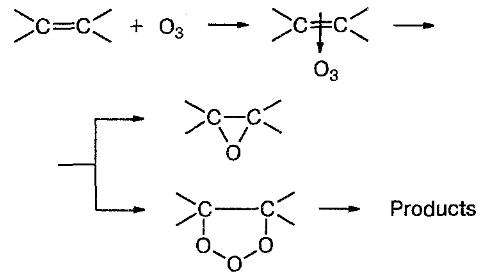
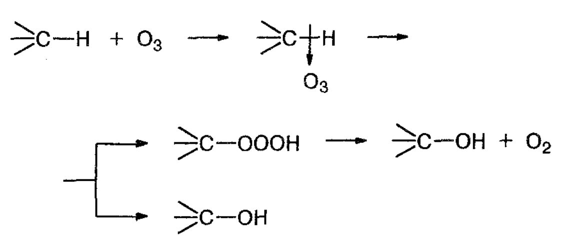
Rate constants for ozone—alkene and ozone—alkane reactions in the gas phase and in solution are compared for 16 hydrocarbons. The gas-phase reactions proceed slower than the reactions in solution. The ratios of the rate constants in the liquid and gas phases differ for ozone—alkene (~17) and ozone—alkane (~2.4) reactions.

Key words: ozone, reaction rates comparison, alkenes, alkanes.

The aggregate state of the system rather often manifests an effect on the reaction rate and mechanism of the chemical process but is insufficiently studied. The kinetics of ozone reactions is studied in both the gas phase[1—9] and in solutions.[10—18] It seems important to find the means for comparison of available data for systems in different phase states.

Two reactions with relatively well studied mechanisms were chosen: the reactions of ozone with olefins and paraffin hydrocarbons. Both reactions are bimolecular at low concentrations of reagents. Their mechanisms are described in detail.[17,19,20] It is noteworthy that the reactions of both systems have the same first stage: the addition of ozone to the reacting group of a substrate.





The addition of ozone is the rate-controlling stage for consumptions of ozone and substrate, which are usually measured during the experiment. This methodical harmony facilitates the comparison of data for different aggregate states of the system.

In choosing the reactions, we paid special attention to their sensitivities to change in the medium polarity. The published data show that the reaction rates depend[11,15] slightly on the polarity or are independent[21,22] of it. This allows us to believe that the differences are caused not by specific solvation or other particular factors, but by universal properties of the medium. The values of the bimolecular rate constants for the reactions of ozone with 16 various representatives of the homologic series of alkenes and alkanes, including linear and branched structures, are presented in Table 1. The reaction center of alkenes is the well localized and rather rigid C=C group, while in alkanes all C—H bonds are reactive. The k_l values for both series were measured under comparable conditions: a bubbling reactor, 20 °C, and CCl_4 as the solvent.

The k_l/k_g ratios presented in Table 1 characterize the differences in reaction rate constants in the gas phase and in solution. It is seen that the averaged k_l/k_g ratios for ozone—alkene and ozone—alkane reactions differ by ~7 times: they comprise 17 and 2.4, respectively. The scatter of the k_l/k_g values is higher for alkenes than for alkanes. This is probably related to the higher error in measurements of high rate constants and the effect of specific features of the olefin structure. However, the available data do not allow one to choose one of these two alternative explanations.

It is noteworthy that fast and slow radical reactions also have different sensitivities to the phase transition. For example, chain propagation reactions of oxidation of cyclohexene and isopropylbenzene exhibit almost the same effect as that mentioned above for the reactions of ozone.

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Table 1. Rate constants of ozone—alkene and ozone—alkane reactions at 20 °C

Compound	Rate constant/L mol^{-1} s^{-1}			k_l/k_g
	$k_g \cdot 10^{-3}$	Ref.	$k_l \cdot 10^{-3}$	
	Alkenes[a]			
Ethylene	1.6	4	40[b]	27
	1.8	23		
	1.0	24		
Propylene	7.1	24	100[b]	14
But-1-ene	6.2	4	130	26
	3.9	23		
trans-But-2-ene	29	9	—	—
	3[	4		
cis-But-2-ene	63	25	163	4.1
	17	23		
Isobutene	14	4	97	19
	3.6	23		
	3.7	9		
2-Methylbut-2-ene	45	4	500	11
Pent-1-ene	3.9	23	190	34
	3.2	3		
	4.5	9		
	Alkanes[c]			
Methane	0.85		—	—
Ethane	1.6[b]		—	—
Propane	4.1		10	2.4
n-Butane	5.9		13	2.2
Isobutane	12.2		150[b]	12.0
n-Pentane	7[b]		15	2.1
n-Hexane	8[b]		19	2.4
3-Methylpentane	60[b]		160	2.7

[a] For k_l see Ref. 16. [b] Obtained by extrapolation of the experimental data. [c] For k_g see Ref. 5; for k_l see Ref. 17.

$$C_6H_{10} + RO_2^{\bullet} \longrightarrow C_6H_9^{\bullet} + ROOH$$

$$k_l = 4.5\ \mathrm{L\ mol^{-1}\ s^{-1}}\ [26]$$

$$k_l/k_g = 40\ [27]$$

$$Me_2CHPh + RO_2^{\bullet} \longrightarrow Me_2C^{\bullet}Ph + ROOH$$

$$k_l = 0.31\ \mathrm{L\ mol^{-1}\ s^{-1}}\ [26]$$

$$k_l/k_g = 8\ [27]$$

An increase in the reaction rate on going from the gas phase to solution agrees with the theory and is first of all associated with an increase in the collision frequency of particles in the liquid compared to the gas phase. However, the real scale of acceleration is unpredicted due to the great number of factors that can be hardly taken into account. It can be mentioned that the calculations based on the increase in the number of collisions[27] overestimate the rate constant by 30—100 times compared to the experimental data, which testifies that the models should be corrected.

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