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NOTES

Catalysis and Inhibition by Water during the Liquid-Phase Oxidation of Hydrocarbons

In the abundant literature on the liquid-phase oxidation of hydrocarbons by dioxygen, many references can be found to the rate-influencing role of water (formed or added during the oxidation). Most of them relate to the inhibitory effect of water when present in high excess. For example, it has been reported that the autoxidation of different alkylbenzenes and α-phenylcarbinols is entirely prevented by an excess of water (*1*, *2*). On the other hand, it has also been stated that, of the polar molecules, water is able to form H-bonds with inhibitors such as phenols and aromatic amines; the inhibiting group is then blocked and the H-bonded inhibitor molecules do not react with the peroxy radicals. The inhibitory activity is therefore diminished, and the overall rate of the inhibited reaction will be increased by the presence of water (*3*).

To the best of our knowledge, no references are in the literature with respect to real catalysis by water in the liquid-phase oxidation of hydrocarbons in the absence of metal ions. In the presence of metal ions, however, water may exert a rate-influencing effect, but this is always connected with the formation of aquo and hydroxo complexes, i.e., the catalytic species is modified. In this paper, we present examples to show that water is a real catalyst when applied in small quantities during the oxidation of hydrocarbons with dioxygen.

The hydrocarbons investigated (tetralin, cumene, cyclohexene, methylcyclohexane, and chlorobenzene) were purified by methods usual for liquid-phase oxidation (*4*). The freshly distilled liquids were dried over Linde 3A zeolite (preactivated by heating at 620K for 5 h) by effective agitation over a period of 24 h. Immediately before use, the liquid (stored above the zeolite) was filtered with a Whatman 1PS silicone-treated phase separator to remove the zeolite particles (as potential heterogeneous catalysts) in a dry box. For each experiment, 8.00 cm^3 of the hydrocarbon and 2.00 cm^3 of the appropriate hydroperoxide solution (prepared with the given hydrocarbon) were measured into the reaction vessel. A thermostatable glass reaction vessel of about 35 cm^3 was fitted with a reflux condenser via ground-glass joints and the condenser was cooled with water at 283 K. At the lower end of the condenser, a small gold receptacle collected the condensed liquid to prevent it from falling back into the reaction mixtures. Water was added with the aid of a precision syringe and the sample was then saturated by bubbling thoroughly dried O_2 through it. The reactor was next attached to a syringe-type thermostated gas burette (Metrohm Dosimat E415P with somewhat modified wiring) previously filled with dried O_2. The reactor was heated up to 343K and the magnetic stirrer was switched on. After heating for 3 min, the measurement of O_2 uptake was started in the dark and the data were stored with the aid of a personal computer. The resulting O_2 uptake vs time curves had the usual autocatalytic shape, with different induction periods; the slope of the longest rising portion of the curve was taken as the initial rate of oxidation.

Figure 1 shows typical curves for the dependence of the rate of oxidation on the quantity of water added. Table 1 lists rate data measured at conditions of three differ-

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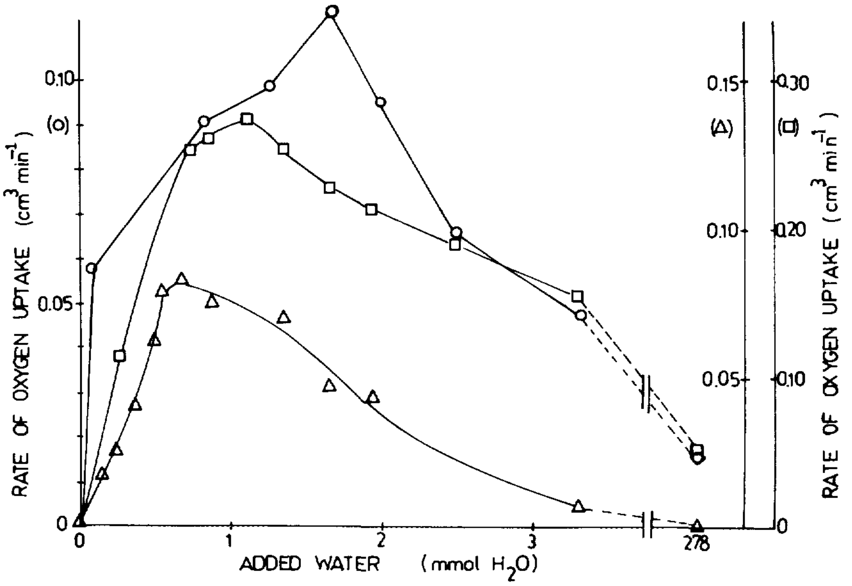

FIG. 1. Rates of oxidation of hydrocarbons as a function of the quantity of water. ○, 7.36 *M* tetralin with 0.0076 *M* THP (left scale). □, 7.36 *M* tetralin with 0.195 *M* TBHP (second right scale). △, 7.85 *M* methylcyclohexane with 0.0069 *M* TBHP (first right scale).

ent quantities of water: (i) in the absence of water; (ii) at $[H_2O]_{max}$, where the maximum rate of oxidation was found; and (iii) in the presence of a large excess of water (5 cm^3, 278 mmol). From these data, it can be concluded that water really does catalyze the oxidation of hydrocarbons, but that the catalysis turns to inhibition or ceases when water is applied in excess, causing the water to form a separate phase. The aromatic and nonaromatic autoxidants behave similarly, but the maximum rate of oxidation is higher in the case of aromatics (Table 1, footnote *a*). The catalysis and inhibition phenomena did not change when these compounds were investigated in chlorobenzene solution (Table 1, footnote *b*). Despite the 1 : 5 dilution, the rate of oxidation remained the same or was even higher. This is probably connected with the fact that the solubility of water is somewhat higher in chlorobenzene (see data in Table 2). The simultaneous application of some phase-transfer catalyst (such as methyltricaprylammonium or tetrahexylammonium chloride) in the reaction mixture (Table 1, footnotes *c* and *d*) did not shift the position of the rate maximum, but the rate was enhanced considerably. This is due to the fact that the onium ions interact with the hydroperoxide and promote the formation of free radicals (*6*, *7*); further, the solubility of water is somewhat increased in the presence of phase-transfer catalysts. It was also found that the oxidation yield depended on the nature of the initiating hydroperoxide. The optimum concentration of water is determined by the initial concentration of hydroperoxide. The rate-influencing effect of D_2O was similar to that of H_2O.

Table 2 gives information about the solubility of water in the pure hydrocarbons used (except for cyclohexene). In the case of cyclohexene, the water content cannot be determined by the Karl Fischer method because cyclohexene reacts with the titrant. It should be considered, however, that the polar component of the investigated systems exerts a water-dragging effect (*8*), i.e., all polar solutes promote the transfer of wa-

TABLE 1

Rates of the Liquid-Phase Oxidation of Hydrocarbons in the Presence of Different Quantities of Water

Hydrocarbon	Initiator/ mmol		$[H_2O]_{max}$/ mmol	Rate of O_2 uptake (cm^3/min) with different water quantities (mmol)		
				0.00	$[H_2O]_{max}$	278
Tetralin[a]	THP	0.076	1.66	0.0	0.115	0.013
Tetralin[a]	TBHP	0.780	0.53	0.034	0.232	0.022
Tetralin[a]	TBHP	1.95	1.12	—	0.274	0.055
Cumene[a]	CHP	0.064	1.66	0.003	0.083	0.0025
Cumene[a]	TBHP	0.140	1.66	0.006	0.132	0.00
Cyclohexene[a]	ChHP	0.063	1.66	0.003	0.137	0.0254
Methylcyclohexane[a]	TBHP	0.068	0.66	0.00	0.082	0.00
Tetralin[b]	THP	0.066	1.66	0.024	0.152	0.00
Cumene[b]	CHP	0.40	1.66	0.004	0.106	0.00
Cyclohexene[b]	ChHP	0.064	1.64	0.01	0.105	0.053
Tetralin[c]	THP	0.076	1.66	—	1.36	0.47
Methylcyclohexane[c]	TBHP	0.069	1.66	0.00	0.1146	0.00
Methylcyclohexane[d]	TBHP	0.069	1.66	0.00	0.087	0.00

Note. THP, tetralin hydroperoxide; TBHP, *tert*-butyl hydroperoxide; CHP, cumylhydroperoxide; ChHP, cyclohexenylhydroperoxide.

[a] 10.00 cm^3 hydrocarbon + water.

[b] 2.00 cm^3 hydrocarbon + 8.00 cm^3 chlorobenzene + water.

[c] As for *a* but plus 0.096 mmol methyltricaprylammonium chloride.

[d] As for *a* but plus 0.10 mmol tetrahexylammonium chloride.

ter molecules associated with them to various extents into the organic solvents.

As to the form of the water molecules transferred into the organic phase, not much is definite. However, the fact that the solubility of water increases with rising temperature in the case of aromatic compounds indicates that the protons of the water molecules interact with the π-electrons of the aromatic ring. This type of complex formation probably counteracts the self-association of water, and as a result the concentration of single and less-associated water molecules in nonpolar aromatic liquids will be higher than that in saturated compounds. If it is now considered that the rate-enhancing effect of water is higher for aromatic compounds than for saturated ones, it can be concluded that the single and/or less-associated water species are the better-activating entities.

In the absence of water, the autoxidation

TABLE 2

Solubility of Water in Various Hydrocarbons[a]

Hydrocarbon	Dissolved water (mmol/10 cm^3 hydrocarbon) at	
	289K	343K
Chlorobenzene	0.313	1.330
Tetralin	0.317	1.168
Cumene	0.221	0.873
Cyclohexane	0.406	0.364
Methylcyclohexane	0.419	0.366

[a] Measurement: 10.00 cm^3 hydrocarbon and 5.00 cm^3 water were effectively mixed in a thermostated glass reaction vessel with a magnetic stirrer for 1 h. The stirring was then stopped and after a separation time of 1 h at the given temperature the organic phase was filtered with a Whatman 1 PS phase separator and its water content was estimated by the Karl Fischer method.

of the investigated hydrocarbons takes place at very low rates, which relates to the fact that the thermal decomposition of hydroperoxide molecules resulting in radicals is very low under the mild experimental conditions used. After the addition of a small quantity of water, the protons of the active water species interact with hydroperoxide molecules and the easier splitting of the O–O bond of the H-bonded hydroperoxide complex furnishes a higher radical concentration for the start of the oxidation chain.

The more active water species will interact with the peroxy radicals, too; in other words, the propagation and termination steps are also influenced by water, which usually results in diminishing rates. However, the overall rate of oxidation is proportional to the term $k_{\text{propag}} \cdot (k_{\text{termin}})^{-1/2}$ (*3*) and consequently the overall rate of oxidation will be influenced only moderately by water via the H-bond interaction of peroxy radicals.

When water is applied in a higher quantity, the concentration of active water species starts to decrease due to their self-association, and hence the radical production will be limited and the overall rate starts to diminish; when water appears as a separate phase, the rate drops to almost the initial low value.

Experiments are in progress to learn more about the nature of the water catalysis of the autoxidation of hydrocarbons.

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