

Promising hydrogen peroxide stabilizers for large-scale application: unprecedented effect of aryl alkyl ketones

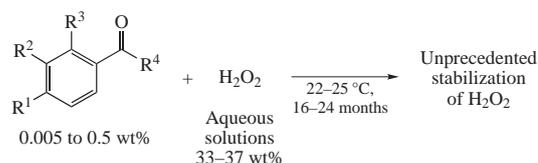
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Aryl alkyl ketones with substituents in the aromatic ring taken in an amount from 0.005 to 0.5% efficiently stabilize hydrogen peroxide in an aqueous solution during storage at 22–25 °C for 16–24 months.



Hydrogen peroxide is one of large-scale products highly demanded in industry and laboratory chemistry. Scientific research related to hydrogen peroxide involves the following three areas of the study: preparation, application, and stabilization. A considerable progress has been achieved in the former two areas.^{1,2} Less advances have been made in investigations concerning the stabilization of hydrogen peroxide, which still remains one of the key problems. Hydrogen peroxide decomposes on storage when exposed to light or high temperatures, and on contact with organic impurities and salts of metals of variable valence.³ Therefore, a common practice is to use stabilizers which can be divided into inorganic and organic ones. Alkaline phosphates, pyrophosphates, phosphate salts,⁴ and tin derivatives⁵ are included in the first group. The second group mainly comprises derivatives of phosphonic acids,⁶ phenol and its derivatives,⁷ sulfonic acids,⁸ citric acid and its salts,⁹ heterocyclic compounds,¹⁰ and surfactants combined with phenylacetic, salicylic, sulfosalicylic, and amino carboxylic acids,¹¹ arenecarboxylic acids in combination with phosphonic acid.¹² High demand for hydrogen peroxide and the diversity of its applications motivates the search for new compounds in order to extend the range of stabilizers. In the present work, when studying the synthesis of organic peroxides from carbonyl compounds and hydrogen peroxide, we unexpectedly found that aryl alkyl ketones would efficiently stabilize aqueous solutions of hydrogen peroxide.

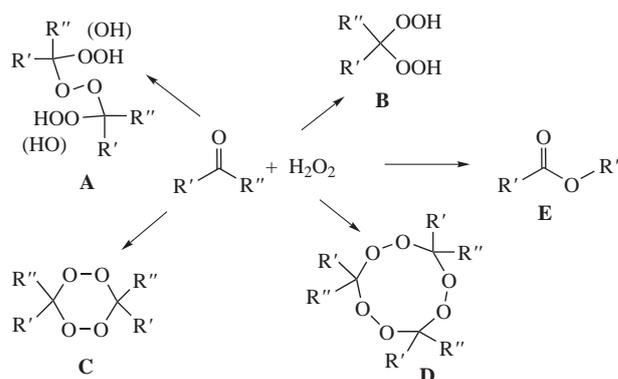
Aryl alkyl ketones are available commercial products which due to low toxicity are used as fragrances in soaps, detergents, cosmetics, and perfumes,¹³ and are the components of grape, cherry and tobacco flavors.¹⁴

We tested aryl alkyl ketones **1–15** with σ -electron-donating, π -electron-withdrawing, and π -electron-donating substituents for the stabilization of hydrogen peroxide (Table 1).[†] Runs 1 and 2 were performed in the absence of aryl alkyl ketone. In these experiments, the hydrogen peroxide concentration substantially decreased (by 15.5 and 23.85%) within 16 and 24 months, respectively. In runs 3–8, we studied the effect of the amount of acetophenone on the change in the hydrogen peroxide concentra-

tion. In the acetophenone concentration range from 0.005 to 0.5 wt% (0.013–1.385 mmol of acetophenone **1** per 1 mol of H₂O₂), a decrease in the hydrogen peroxide concentration was almost the same (was not higher than 0.7%). Other aryl alkyl ketones **2–5** with substituents in the aromatic ring also exert a strong stabilizing effect. In the cases of 0.5 wt% concentration of aryl alkyl ketones (0.924–1.291 mmol of **2–5** per 1 mol of H₂O₂), the loss of the hydrogen peroxide concentration was not higher than 0.35% at 22–25 °C for 16 months (runs 9–12).

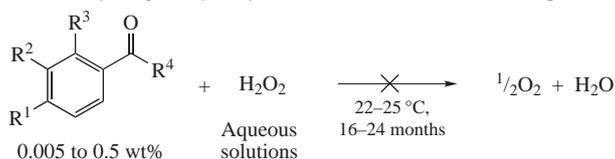
Under similar conditions, we tested a series of acetophenones **6–15** with π -electron-donating substituents. A decrease in the hydrogen peroxide concentration was observed in all cases (runs 13–22). For methoxyacetophenone **6**, the concentration loss was 10.55% (run 13), and the decrease in the hydrogen peroxide concentration in the presence of hydroxyacetophenones **7–9** varied from 10.15 to 13.10% within 16 months (runs 14–16). For halogen-substituted acetophenones **10–15**, the loss of the concentration was in the range from 5.93 to 15.50% (runs 17–22).

The application of ketones as stabilizers is the key finding in this work. In industry and laboratory practice, ketones are traditionally used as the reactants with hydrogen peroxide to prepare organic peroxides, for example, linear peroxides **A**¹⁵ and **B**¹⁶ and cyclic peroxides **C**¹⁷ and **D**,¹⁵ and are also oxidized to form esters **E**^{16(b),18} (Scheme 1).



Scheme 1

[†] For details, see Online Supplementary Materials.

Table 1 Effect of the nature of substituents in the aryl ring of aryl alkyl ketones on the stabilization of aqueous solutions of H₂O₂.

Run	Aryl alkyl ketone 1–15	R ¹	R ²	R ³	R ⁴	Mass (1–15)/ mass of solution (wt%)	Molar ratio, mmol of 1–15/ mol of H ₂ O ₂	Initial concentration of H ₂ O ₂ (wt%)	Final concentration of H ₂ O ₂ (wt%)	Loss of H ₂ O ₂ (wt%)	Time/ months
1	None	–	–	–	–	0	0	36.75	21.25	15.50	16
2	None	–	–	–	–	0	0	36.75	12.90	23.85	24
Aryl alkyl ketones with σ-electron-donating and π-electron-withdrawing substituents exerting pronounced stabilizing effect											
3	1	H	H	H	Me	0.5	1.385	33.63	33.30	0.33	16
4	1	H	H	H	Me	0.5	1.385	33.63	33.10	0.53	24
5	1	H	H	H	Me	0.2	0.560	34.15	33.55	0.60	24
6	1	H	H	H	Me	0.1	0.280	34.40	33.75	0.65	24
7	1	H	H	H	Me	0.05	0.133	33.80	33.18	0.62	24
8	1	H	H	H	Me	0.005	0.013	35.00	34.33	0.67	24
9	2	Bu ^t	H	H	Et	0.5	1.291	36.82	36.60	0.22	16
10	3	Me	H	H	Me	0.5	1.068	36.84	36.55	0.29	16
11	4	C(O)Me	H	H	Me	0.5	1.059	36.82	36.47	0.35	16
12	5	H	H	COOH	Me	0.5	0.924	36.82	36.52	0.30	16
Aryl alkyl ketones with π-electron-donating substituents exerting weak stabilizing effect											
13	6	OMe	H	H	Me	0.5	1.153	36.80	26.25	10.55	16
14	7	OH	H	H	Me	0.5	1.259	36.82	26.37	10.45	16
15	8	H	H	OH	Me	0.5	1.272	36.82	26.67	10.15	16
16	9	OH	H	OH	Me	0.5	1.143	36.82	23.72	13.10	16
17	10	H	H	Cl	Me	0.5	1.130	36.84	28.82	8.02	16
18	11	Cl	H	H	Me	0.5	1.113	36.82	30.89	5.93	16
19	12	Cl	H	Cl	Me	0.5	0.920	36.82	27.67	9.15	16
20	13	H	Br	H	Me	0.5	0.883	36.82	30.10	6.72	16
21	14	Br	H	H	Me	0.5	0.875	36.80	27.46	9.34	16
22	15	OMe	Br	H	Me	0.5	0.760	36.80	21.30	15.50	16

In reactions with acetophenones used in the present study, hydrogen peroxide can add to the carbonyl carbon atom, however, the equilibrium is substantially shifted toward the starting compounds. In our previous study, the peroxidation of acetophenone was observed in low yield only under strongly acidic conditions.¹⁹ The probable mechanism of the consumption of the stabilizer involves the generation of the hydroxyl radical from hydrogen peroxide followed by the hydrogen atom abstraction by this radical from the methyl or methylene group of aryl alkyl ketone to give a C-centered radical. The formation of the latter from ketones in reactions with peroxides is a known process employed in preparative organic synthesis.²⁰ In addition, hydrogen peroxide is consumed in subsequent oxidative transformations of C-centered radicals. Substituents having π-electron-donating properties promote oxidative transformations to a greater extent compared to σ-electron-donating and π-electron-withdrawing substituents. The presence of products of the multistep oxidation of ketones to the corresponding benzoic acids in the reaction solution after 16–24 months was confirmed by GLC. Thus, 3-bromobenzoic acid was produced from 3-bromoacetophenone **13**; 4-chlorobenzoic acid, from 4-chloroacetophenone **11**; 4-methoxybenzoic acid, from 4-methoxyacetophenone **6**. These benzoic acids were also characterized by NMR spectroscopy.[†]

In conclusion, aryl alkyl ketones, including those with both electron-donating and π-electron-withdrawing substituents, are proposed as new stabilizers of aqueous solutions of hydrogen peroxide. The efficient stabilizing effect is observed within 16–24 months for 33–37% H₂O₂ in the presence of a stabilizer in an amount of 0.005–0.5 wt% of the weight of the solution. Taking into account the large scale of application of hydrogen

peroxide, as well as the commercial availability and low toxicity of aryl alkyl ketones, the results of the present study can find use in industry.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.021.

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