

was filtered, washed with NaOH (10%), water, and all common solvents, including Me₂SO, and weighed: 0.48 g; mp >250 °C.

Photostimulated Reactions of Halophenyl *N,N*-Disubstituted Amide Enolate Anions. To an equimolecular amount of amide ions in liquid ammonia was added the substrate, and after the time indicated in Table III, the reaction was quenched with water. The residue obtained was insoluble in most common solvents but was soluble in Me₂SO and was precipitated by addition of water, giving a fine powder, mp 180–200 °C.

Registry No. 1a, 106-46-7; 1b, 106-37-6; 1c, 589-87-7; 2a, 24262-31-5; 2b, 64723-95-1; 3b, 74824-50-3; 5, 74824-46-7; 7, 35337-68-9; 8, 74824-47-8; 9, 74824-48-9; *N*-(*p*-chlorobenzyl)acetamide, 57058-33-0; *p*-chlorobenzylamine, 104-86-9; *N*-methyl-*N*-(*p*-chlorophenyl)acetamide, 10219-10-0; 1,4-bis[(2-propenyl)oxy]benzene, 42237-99-0; 1,4-bis[(3,3-dimethyl-2-butenyl)oxy]benzene, 74824-49-0; *p*-chlorothiophenol, 106-54-7; chlorobenzene, 108-90-7.

Removal of Peroxide Impurities by Zeolites

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The literature¹ provides a large number of chemical methods, mainly of a reductive nature, for the removal of peroxides from reagents or solvents, including treatment with alkalis, sodium sulfite, ferrous sulfate, stannous chloride, lead dioxide, zinc and acid, sodium and alcohol, lithium aluminum hydride, and triphenylphosphine. A disadvantage of these methods is the time required, as additional purification by distillation and/or drying is necessary. Moreover, in the case of tetrahydrofuran containing a high concentration of peroxides, the application of some of these methods can be dangerous.^{2,3}

Relatively little attention has been paid to the removal of peroxides by selective adsorption. It has been reported that the peroxide content can be reduced by passing the reagent/solvent down an alumina column.⁴ We observed, as part of an investigation of the zeolite-catalyzed hydrobromination of alkenes,⁵ that peroxide impurities of the alkene compound were selectively adsorbed by zeolites. The extent of adsorption was found to depend on the type of zeolite; with zeolite NaX a fast and essentially complete adsorption was observed. A close examination of the literature revealed that the use of NaX pellets has been suggested for the removal of moderate quantities of peroxides from tetrahydrofuran, but no quantitative data were presented.⁶

Since with NaX side reactions are not expected to occur due to its weak acidity and/or the absence of catalytically active cations, the use of NaX was investigated in more detail.⁷ For comparison experiments were performed with

basic alumina. Typical peroxide-containing solvents like tetrahydrofuran and diisopropyl ether and reagents known to be susceptible to hydroperoxide formation like cyclohexene and 1-octene were used as test substrates. The peroxide oxygen content was quantitatively determined by a photometric ferric thiocyanate method.⁸

Table I shows the results obtained when the reagents were treated with the adsorbent in a slurry technique. With zeolite NaX a strong reduction of the peroxide content of tetrahydrofuran and diisopropyl ether was obtained, whereas cyclohexene and 1-octene became nearly peroxide free. Gas-chromatographic analysis showed that no isomerization of 1-octene occurred. It may be mentioned that drying tetrahydrofuran with zeolite NaA pellets also resulted in some reduction of the peroxide content, showing outer surface adsorption on the zeolite pellet.

For basic alumina a similar order for the removal of peroxides was observed as with NaX. Here good results were obtained for cyclohexene and 1-octene, but only if physically adsorbed water was removed by calcination at 250 °C. For the ethereal solvents the application of a slurry technique using alumina seems less suitable. Therefore, some experiments were performed where these solvents were passed down a column of adsorbent.

When NaX is used in a column technique (see Figure 1) an efficient removal of peroxides was observed. Though not shown in the figure, for tetrahydrofuran (peroxide content 177 μmol/L) a breakthrough was observed after 400 mL, showing an effective use of adsorbent of 0.6% w/v. Initially alumina also gives good results when applied in a column, but its adsorption capacity is much smaller than that of NaX.

The reduction of the peroxide content with NaX may be caused by selective adsorption and/or by decomposition of the peroxides. Some experiments were performed in which an equal volume of methanol or ethanol was subsequently added to the slurry to desorb the adsorbed species in order to find out which phenomenon predominates with NaX, using a slurry technique. It appeared that in this way the greater part of the peroxides was recovered by desorption, showing that the removal of peroxides by NaX is mainly caused by physical adsorption into the zeolite.

It is known that certain zeolites induce decomposition⁹⁻¹³ of peroxides. An exploratory series of experiments were performed with zeolite Co(II)X as the adsorbent in order to see whether such decomposition improves the purification of peroxide-contaminated solvents. Slightly improved peroxide removal was obtained, as shown by the data in Table II. With 1-octene traces of 2-octenes were observed after treatment with CoX, showing the isomerization activity of CoX. In contrast to NaX, recovery of the removed peroxides upon addition of methanol or ethanol was very low, showing that with CoX adsorption of the peroxides is followed by a decomposition of the adsorbed species. For instance, cyclohexene α-hydroperoxide was found to yield 2-cyclohexene-1-ol and 2-cyclohexen-1-one upon treatment with CoX. Both decomposition products adsorb selectively with respect to cyclohexene into zeolite CoX.¹⁴

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Table I. Removal of Peroxides by Zeolite NaX and Alumina

solvent	peroxide content, $\mu\text{mol/L}$	fraction (%) removed by ^a		
		NaX ^b	Al ₂ O ₃ ^c	Al ₂ O ₃ ^d
tetrahydrofuran	177	90	34	68
diisopropyl ether	442	92	10	57
cyclohexene	300	99	57	95
1-octene	25375	>99.9	80	99

^a Solvent and adsorbent (10% w/v) were stirred for 15 min at room temperature. ^b Powder calcined at 400 °C. ^c Not calcined. ^d Calcined at 250 °C (surface area 118 m²/g).

Table II. Removal of Peroxides by CoX

solvent	peroxide content, $\mu\text{mol/L}$	fraction	
		removed, % ^a	recovered, % ^b
tetrahydrofuran	163	92	15
diisopropyl ether	372	94	14
cyclohexene	265	99	10
1-octene	6975	>99.9	1

^a Solvent and zeolite powder CoX (10% w/v, calcined at 400 °C) were stirred for 15 min at room temperature.

^b After addition of an equal volume of methanol (in the case of 1-octene-ethanol) to the slurry.

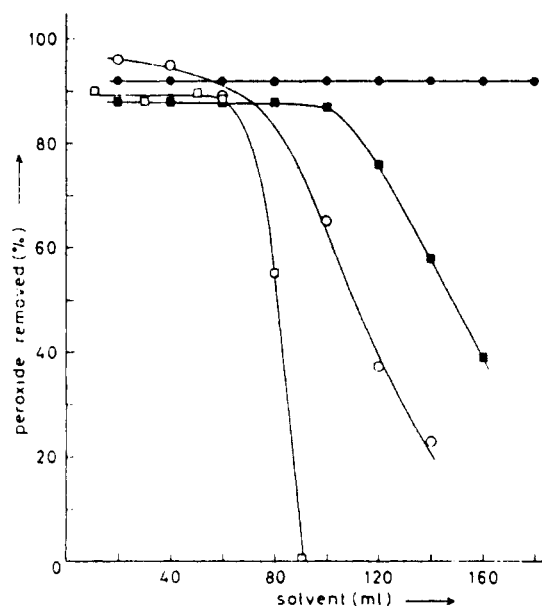


Figure 1. Removal of peroxides from tetrahydrofuran (O, ●) and diisopropyl ether (□, ■) at room temperature by passing these solvents over 5 g of basic alumina, calcined at 250 °C (O, □), and over 2.5 g of NaX (ground pellets, 0.1 < *d* < 0.15 mm), calcined at 400 °C (●, ■); flow rate 2–3 mL/min; initial peroxide content of tetrahydrofuran 177 and of diisopropyl ether 442 $\mu\text{mol/L}$.

Additional experiments showed that treatment of a solution of *tert*-butyl hydroperoxide in a hydrocarbon solvent with CoX resulted in the formation of *tert*-butyl alcohol and the evolution of a substantial amount of oxygen (molar ratio oxygen/peroxide 0.25 in cyclohexane and 0.45 in benzene). ESR spectroscopy of CoX showed nearly similar spectra before and after the reaction with hydroperoxide, indicating that most cobalt ions remain divalent. This can

be understood in terms of the known oxidation–reduction processes of cobalt ions in the homogeneously catalyzed decomposition of hydroperoxides.^{15–18} In view of these results the mechanism of the zeolite-catalyzed decomposition of hydroperoxides is under further investigation.

In conclusion, zeolite X used in a slurry or column technique may serve as a convenient method for reduction of the peroxide content of solvents and reagents. Especially for apolar reagents like alkenes an essentially complete removal is obtained.

Experimental Section

Pure grade reagents and solvents were used. Zeolite NaX, powder and pellets, was obtained from Union Carbide, basic alumina 80–200 mesh from Fisher. Zeolite CoX was obtained from NaX by conventional ion-exchange techniques; 64% of the Na ions were replaced by Co(II) ions. The zeolites were calcined in air at 400 °C and the alumina at 250 °C (weight loss 5.2%).

Techniques. When a slurry technique was applied, 10 mL of reagent was stirred with 1 g of adsorbent at room temperature. After 15 min the slurry was centrifuged¹⁹ and the peroxide content of the solution was determined. For column chromatographic experiments a column (diameter 1 cm) was filled with dry adsorbent and the solvent was passed down the column with a flow rate of 2–3 mL/min. Portions of 10 mL of treated solvent were collected and the peroxide content was determined. In view of the small particle size of NaX powder, ground pellets (0.1 < *d* < 0.15 mm) were used for column chromatography.

Analysis. Solutions of ferrous chloride and of ammonium thiocyanate were prepared as described by Smith.⁸ Samples (20–1000 μL) of the reagents were solved in methanol, the volumes were made up to 10 mL, and 0.1 mL of a freshly prepared mixture (1:1 v/v) of the ferrous chloride and ammonium thiocyanate solutions was added. The intensity of the red color which developed was measured with a Perkin-Elmer 402 ultraviolet–visible spectrophotometer at 515 nm. After calibration of the spectrophotometer,²⁰ the readings were converted to micromoles of peroxide oxygen.

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Registry No. Alumina, 1344-28-1; tetrahydrofuran, 109-99-9; diisopropyl ether, 108-20-3; cyclohexene, 110-83-8; 1-octene, 111-66-0.

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(14) After a solution of 2-cyclohexen-1-ol (0.35 g L⁻¹) and 2-cyclohexen-1-one (0.8 g L⁻¹) in cyclohexene with CoX (100 g L⁻¹) was slurried, residual concentrations of cyclohexenol and cyclohexenone amounted to 5 mg L⁻¹ and 50 mg L⁻¹, respectively, as determined by GC analysis using 1,3,5-tri-*tert*-butylbenzene as internal standard.