Oligomer model to explain the coloration of TEA and discoloration catalytic treatment

C. Longuet [a], B. Coq [a], R. Durand [a], A. Finiels [a], P. Geneste [a,*], M. Mauvezin [b]

[a] Laboratoire des Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS-ENSCM-UM1, Institut C. Gerhardt FR 1878,
8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France
[b] Centre de Recherche BP, 13117 Lavera, France

Abstract

To understand origin of the undesirable well-known coloration of triethanolamine by compounds at trace levels, a model of insaturated oligomers is proposed. The hydrogenation in the presence of various supported metal catalysts is an attractive process for TEA discoloration, and a 5 wt.% Pd/C catalyst exhibited the highest efficiency.
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1. Introduction

Ethanolamines, including monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA), offer a broad spectrum of application opportunities. Because ethanolamines combine the properties of amines and alcohols, they exhibit a unique capability of undergoing reactions common to both groups. Ethanolamines are conventionally prepared by reacting at 50–60 °C ethylene oxide with aqueous ammonia in a SN2-type reaction. Freshly prepared ethanolamines are water-white liquids.

Triethanolamine, obtained by fractional distillation of the ethanolamine crude product, is widely used as an ingredient in emulsifiers, thickeners, wetting agents, detergents and alkalinizing agents in cosmetic products, as a chemical intermediate for anionic and nonionic surfactants and surface active agents, as a vulcanization accelerator in the manufacture of rubber and in many other industrial applications.

It is known that initially colorless pure triethanolamine can after a storage time gradually turn pale yellow and ultimately can turn yellow to brown if left to stand in light, air or in warm environments. Because of its widespread use in cosmetics and other consumer products, such a coloration is wrong and not commercially acceptable. To solve the problem, a recent patent claimed a process for improving the color quality of alkanolamines by treating with hydrogen in the presence of a hydrogenation catalyst [1]. But very little research on the nature of the undesirable compounds has been reported [2] certainly because these degradation products are heavy organic molecules at trace levels and consequently extremely difficult to detect and identify.

The aim of this study is to gain insight regarding the reaction mechanisms for the formation of various degradation compounds from triethanolamine, to choice a model representative of the colored products and to propose an efficient catalytic process to drastically decrease this coloration.

From literature [2,3], one may anticipate that by-products which cause coloration proceed from decomposition of TEA to ethanolamine and acetaldehyde through DEA (Scheme 1). Generally, primary amines as MEA can add to acetaldehyde to give aldimine (Scheme 2); but the reaction, in general, gives polymeric material [4,5] because the aldimine initially formed very easily undergoes subsequent aldol condensation as shown in Scheme 3, and so on. The presence of a double

Scheme 1.

Scheme 2.

bound C=C in addition of the double bond C=N leads to the instability of imines [6].

In turn, similar oligomers can also be obtained via unsaturated aldimine formed from MEA and crotonaldehyde. In fact, acetaldehyde in basic media (MEA is a strong base, $K = 3.39 \times 10^{-10}$) condenses to form crotonaldehyde (Scheme 4).

When a secondary amine as DEA is added to acetaldehyde, the initially formed N,N-disubstituted hemiaminal is unstable and a stable enamine is formed by dehydration (Scheme 5). Based on this ability of reactivity, DEA is considered as a stabilizing species preventing oligomer formation and thence

an ulterior coloration. As a matter of fact, such a positive effect of DEA is used by manufacturers.

It comes clear from previous considerations that acetaldehyde formed from TEA decomposition undergoes further transformations responsible for the formation of compounds which cause the undesired coloration. To get an absorption in UV region, the molecules have to possess insaturated chromophor groups such as HC=N or C=C groups. But then, the conjugaison of multiple bonds results in a shift of the absorption maximum from UV to the visible region and the extinction coefficient is increased, consequently a coloration appears. For example, polyenic aldehydes, $-(HC=CH)_n-COH$, absorb at 312 nm with ε_{max} 40,000 if $n = 3$ and at 415 nm with ε_{max} 63,000 if $n = 7$ [7]. It is obvious that even if these species are present in a very low concentration, the mixture switches to be colored. The same behavior appears in our case.

Scheme 3.

Scheme 4.

Scheme 5.

Our objective is to use a molecule model, or an oligomer model, which accounts for coloration of TEA. In the present study, taking into account the TEA degradation process previously described, we have chosen as model oligomers formed from the reaction of crotonaldehyde with MEA of the general formula:
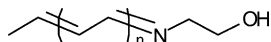
We have then studied the efficiency of supported metals for the catalytic discoloration of TEA, i.e. the hydrogenation of this model oligomer.

2. Experimental

The active carbon-supported precious metal catalysts were purchased from Alfa Aesar (50% aqueous slurry of 5 wt.% Pd/C, 5 wt.% Pt/C, 5 wt.% Ru/C, references 038.300, 038.321, 011.748, respectively), and a sponge Ni catalyst from Strem (reference 28-1890, 50% aqueous slurry). Because the hydrogenation reaction was conducted in pure TEA, the catalysts were used without any further activation before the catalytic run. The choice of these metals were motivated by their wide ability for hydrogenating C=C, C=N and C=O doubles bonds; Pd being particularly efficient in conjugated C=C–C=C double bonds hydrogenation [8]. The reactants were crotonaldehyde (Aldrich, purity > 99%), monoethanolamine (Aldrich, purity > 99%), and the so-called "pure" TEA as received from the pilot plant (purity ≥ 99%).

Hydrogenation experiments were carried out in a jacketed 100 ml magnetically stirred stainless steel autoclave (Autoclave Engineer) operating in batch mode. The magnetic stirrer operates at a speed of 1000 rpm. In a typical experiment, the autoclave was loaded with 70 ml of the solution to be hydrogenated and 100 mg of supported metal catalyst (or 200 mg of Ni sponge). The autoclave was extensively purged with hydrogen and finally filled with hydrogen to the required pressure (2 MPa) and heated at 343 K for 1 h 30 min.

The extent of the solution coloring was characterized by the APHA color number according to the Dr. Lange's method [9]. The APHA color number is determined from the absorption spectra of the solution at four wavelengths: 430, 455, 480 and 510 nm. A colorless product has a color number inferior to 20 APHA according to DIN-ISO 6271 standart [9]. In order to follow the extent of hydrogenation and hence of discoloration, samples were withdrawn periodically and analyzed by visible spectrophotometry (UVIKON XL Bio-Tek Instruments).

3. Results and discussion

In order to achieve a higher sensitivity in the developing discoloration test, a thermal treatment of "pure" TEA at 453 K for 2 h was carried out for increasing oligomer concentration and intensifying color.
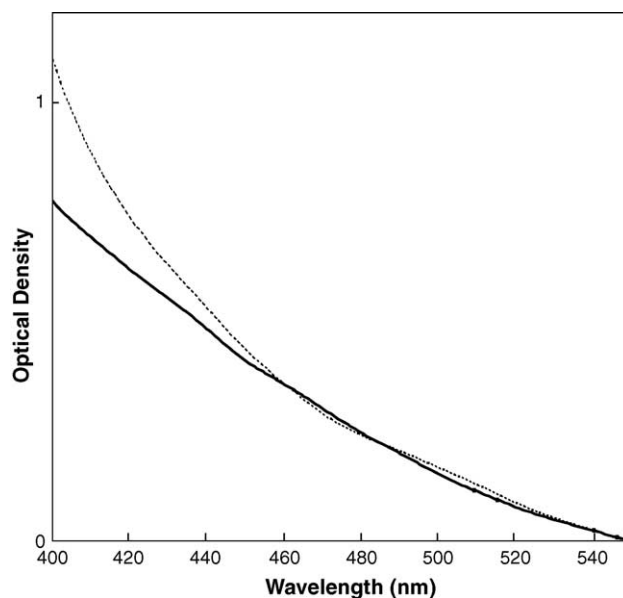

Fig. 1. Visible spectra of solution REF (- - -) compared to thermally aged TEA (—).

The validity of modeling TEA coloration by the formation of oligomers from MEA and aldehydes was further checked by reacting 1.6 mmol MEA (0.1 g) with 1.6 mmol crotonaldehyde (0.113 g) in 70 ml EtOH at room temperature. A colored solution is obtained called solution REF which exhibits a visible spectrum nicely superimposed with that of the thermally aged TEA (Fig. 1); in particular from 450 to 550 nm, the two spectra are identical which indicates a good choice for the model oligomers responsible of coloration. The APHA color number of solution REF is of 150–200. The potential involvement of ethanol itself in the coloring process of solution REF was checked by reacting crotonaldehyde and MEA in the "pure" TEA. The APHA color number thus obtained was very close (120–200) to that of solution REF providing evidence that ethanol does not intervene in the process.

All attempts to identify by GC and GC-MS coupling the products responsible for coloration were unsuccessful.

The hydrogenation of solution REF, "pure" TEA and thermally aged TEA was then carried out on the various catalysts. The progress of discoloration, i.e. the hydrogenation of conjugated double bonds, was followed by periodically withdrawing sample aliquots. A time history plot exemplify in Fig. 2 the discoloration using the 5 wt.% Pd/C catalyst. The APHA color number after 90 min hydrogenation of the solution REF and "pure" TEA over different catalysts are given in Table 1. Because high surface area active carbons are efficient materials for the removal by adsorption of organic compounds from wastes, a blank experiment was carried out with a metal-free active carbon (Norit, high surface area). No significant discoloration was observed in that case providing evidence that the support does not contribute directly in the discoloration process.
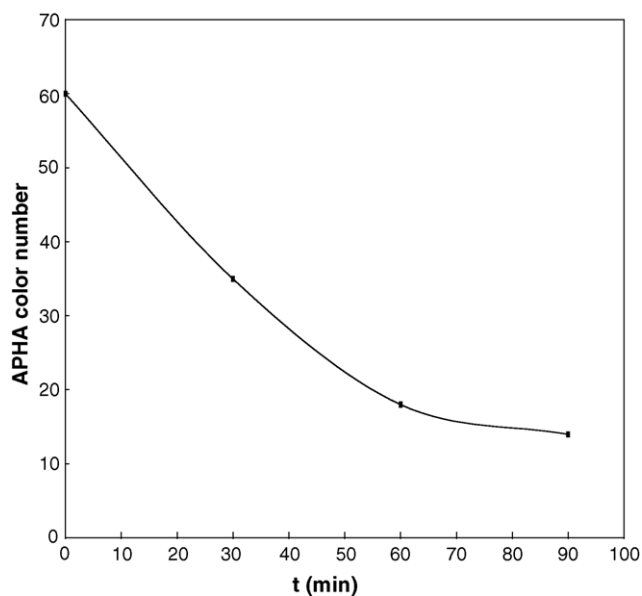
Fig. 2. Time history plot of the discoloration of "pure" TEA on the 5 wt.% Pd/C catalyst.

The Ni sponge catalyst gives an acceptable discoloration of the solution REF but appears slightly less efficient for discoloration of TEA. Moreover, though appearing as a good catalyst, it does not belong to the most preferred materials (Pd and Pt) due to leaching of Ni in the TEA solution [1]. Traces of Ni are generally found in the reaction product because the ethanolamines act as complexing agents toward nickel. These Ni traces are undesired for certain applications, such as cosmetics.

With Ru/C as catalyst, the hydrogenated solution is still yellow in the case of solution REF and more colored in the case of TEA. Ru is known as a powerful hydrogenolytic metal for C−C, C−N bonds [10]. We thus postulate that hydrogenolysis of TEA and DEA to MEA may occur in the presence of such a catalyst; MEA being the precursor favoring the formation of colored oligomers.

Pd/C and Pt/C are the most efficient catalysts for hydrogenation of the by-products responsible of coloration, and they were indeed claimed for that process [1]. However, if Pt/C is as efficient as Pd/C for discoloration of solution REF, it appears less active to discolor "pure TEA". It has been reported that Pt metal is sensitive to poisoning (inhibition) by amines [11]; one may propose that MEA, DEA or NH$_3$ present in the solution, even in trace amounts, inhibit to some extent the hydrogenation activity of Pt/C in comparison with Pd/C.

In conclusion, the Pd/C catalyst appears the most attractive material for an efficient discoloration of a real TEA solution. Moreover, no trace of Pd was detected in the TEA solution after the hydrogenation treatment.

We turned then the attention to the efficiency of the catalytic treatment by Pd/C on a deeply colored TEA solution (a long-time thermally aged TEA). The initial APHA color number of 500–600 was thus remarkably decreased to 10–20 for the hydrogenated solution, as low as for a "pure" TEA solution. This achievement proves the wide applicability of the catalytic treatment to variously colored TEA solutions.

The relative efficiency of the various metals, Pd > Pt > Ni > Ru, is an indirect indication for the good choice of polyconjugated C=C and C=N bonds for the model compounds responsible of the coloration. It is indeed well known that Pd is the most active metal for the hydrogenation of dienes in the liquid phase [12].

4. Conclusion

In summary, we have proposed a model solution obtained by action of crotonaldehyde on MEA which may account to a large extent for the coloration process of TEA. In the hydrogenation of the model solution and comparison with a TEA solution itself using various supported precious metal catalysts, a 5 wt.% Pd/C proves to be the most efficient catalyst for TEA discoloration.

Table 1
APHA color number at the end of the hydrogenation treatment of solution REF and "pure" TEA over various supported metal catalysts

Treated solution	Catalyst			
	Ni sponge[a]	Pd/C[b]	Pt/C[b]	Ru/C[b]
Sol. REF[c]	20–30	0–10	0–10	60
"Pure" TEA[d]	30–40	10–20	40–50	90–100

[a] 0.2 g.
[b] 0.1 g.
[c] Initial color number: 150–200.
[d] Initial color number: 60.

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