

The Thermal Degradation of Model Compounds of Amine-Cured Epoxide Resins. I. The Thermal Degradation of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

J. C. PATERSON-JONES and V. A. PERCY, *Council for Scientific and Industrial Research, Somerset West, Cape, South Africa*, and
R. G. F. GILES and A. M. STEPHEN, *Department of Chemistry, University of Cape Town, Rondebosch, Cape, South Africa*

Synopsis

The thermal degradations of 1-(N-ethylanilino)-3-phenoxypropan-2-ol in an inert atmosphere, in air, and over alumina were studied with the aim of investigating the thermal stability of the cure linkage in aromatic amine-cured bisphenol A-based epoxide resins. Degradation products were characterized. Possible degradation mechanisms are outlined and are related to the results of previous studies of the thermal degradation of these resins.

INTRODUCTION

The thermal stability of epoxide resins has been the subject of considerable research. Water has been identified as a major product of the degradation of aromatic amine-cured resins.¹⁻⁸ It has been suggested⁸ that initial degradation involves the formation of water,⁷ hydrogen, and methane by a process which does not involve a breakdown of the resin network. Phenolic, N-methylanilino, N,N-dimethylanilino, and benzofuryl compounds have been observed^{6,7} as major products in the low-temperature (300°C) degradation of the adduct of the diglycidyl ether of bisphenol A and *p,p'*-diaminodiphenylmethane. The breakdown of the resin network has been postulated to occur at the reacted glycidyl group,^{3,4,6-8} at the isopropylidene linkage in the bisphenol A portion of the network,^{3,4,6-8} and at aliphatic portions of the hardener.^{6,7} Bowen⁹ and Bishop and Smith⁸ have shown that the reacted glycidyl group is less stable than the isopropylidene linkage and that initial rupture is most likely to occur at this group.

This paper reports a study of the degradation of a model compound for the cure linkage in aromatic amine-cured bisphenol A-based resins.

EXPERIMENTAL

Analytical Techniques

A Pye Series 105 Model 15 preparative gas-liquid chromatograph (GLC) with a 4.57 m \times 0.953 cm diameter glass preparative column packed with 25% polyethylene glycol (PEG) 20M on 60-72 mesh silanized Celite was used for the separation and identification of products. Permanent gases, low molecular weight aliphatic hydrocarbons, and high molecular weight or polymeric materials were not detected, and no attempt was made to isolate or to identify these compounds.

The operating conditions for each chromatogram were approximately constant: operating temperature, 180-181°C; carrier gas (N₂) flow rate, 206.9 ml/min; column pressure, 30-31 psi; detector, flame ionization.

Retention times which were measured from the time of injection of the samples were corrected against the retention times of standard compounds. Corrected retention times were calculated by

$$t_c = t \times t_s/t_s'$$

where t_c = corrected retention time, t = measured retention time, t_s = actual retention time of standard, and t_s' = measured retention time of standard. The retention times of standard compounds¹⁰ are given in Table I.

A mass spectrometer coupled to a Perkin-Elmer Model 990 gas-liquid chromatograph provided mass spectra of individual components of mixtures of degradation products. (This work was performed by Mr. P. R. Boshoff, Department of Chemistry, University of Stellenbosch, Cape, South Africa.)

TABLE I
GLC Retention Times of Standard Compounds

Compound	Retention time, min	Compound	Retention time, min
Acetaldehyde	1.5	N,N-Diethylaniline	18.0
Acetone	1.8	3-Methylbenzofuran	18.1
Ethanol	1.9	2-Chromene	22.1
Benzene	2.4	N-Ethylaniline	24.6
1-Propanol	2.5	Chroman	25.9
Toluene	3.1	N-Allyl-N-ethylaniline	26.6
Ethylbenzene	3.9	3-Chromene	30.7
Styrene	5.7	Benzyl alcohol	38.5
Phenyl vinyl ether	7.0	Phenoxyacetone	46.1
Anisole	7.3	N-Ethyltetrahydroquinoline	54.0
Phenetole	8.1	Phenol	57.2
Benzofuran	12.9	N-Ethylindole	61.8
Benzaldehyde	13.8	3-Methyl-N-phenylpyrrole	66.1
N,N-Dimethylaniline	14.8	1-Phenoxypropan-2-ol	68.1
2-Methylcoumaran	15.8	N-Ethylskatole	78.9
N-Ethyl-N-methylaniline	17.0	<i>o</i> -Allylphenol	96.7
2-Methylbenzofuran	17.4		

The Synthesis of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

Phenyl glycidyl ether (97.3 g; 0.65 mole) and N-ethylaniline (78.5 g; 0.65 mole) in ethanol (75 ml) were heated under reflux at 100°C for 4 hr. The solution was distilled under reduced pressure and the product was collected as a pale yellow syrup (138.6 g; 78.9%), bp 198–200°C/1.1 mm Hg (lit.¹¹ bp 156°C/0.1 mm Hg).

ANAL. Calcd for $C_{17}H_{21}NO_2$: C, 75.3%; H, 7.7%; N, 5.2%. Found: C, 75.0%; H, 7.7%; N, 5.1%.

Degradation Procedure

1-(N-Ethylanilino)-3-phenoxypropan-2-ol was heated in a conventional glass apparatus which allowed the products to be distilled and collected during the degradation. Degradation was carried out under two conditions:

1. Catalyzed degradation: over aluminum oxide "Camag" M.F.C. Brockmann activity 1 (pH 6), 100–240 mesh.

2. Uncatalyzed degradation: (a) under nitrogen and (b) in air.

Prior to degradation over alumina, the catalyst (50% w/w) was heated for 2 hr at 150°C under vacuum. In degradation 2a, the reaction flask was purged with nitrogen for 15 min before degradation, and a small flow of nitrogen was continued during the degradation. Heating was maintained at such a rate that the temperature of the distilling products did not exceed 250°C. After a certain period, no further products could be distilled at temperatures below 250°C, and heating was discontinued. As a measure of the relative ease of degradation, the time required for degradation was recorded (Table II). After degradation, a highly viscous residue remained. The distillate was separated into neutral, basic, and acidic fractions for identification of its components.

Certain products were collected by preparative GLC. N-Ethylskatole was identified by a comparison of its GLC retention time and its IR, PMR, and mass spectra with those of a standard. The structure of 3-methyl-N-phenylpyrrole was inferred¹⁰ from its IR, PMR, and mass spectra. The remaining compounds (except for 2-chromene) were identified by a comparison of their retention times and mass spectra (where available) with those of standard compounds. The identity of 2-chromene was established by its mass spectrum which was identical with that of 3-chromene.

TABLE II
Data on the Degradations of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

Degradation procedure	Time of degradation, min	Yield of products, % w/w
1	40	65
2a	50	28
2b	45	36

RESULTS

Degradation Products

The products of degradations 2a and 2b were identical in nature and relative abundance, and differed in some respects from those of degradation 1. Degradation products and their means of identification are listed in Tables III and IV. GLC traces of the total products of the degradations are shown in Figures 1 and 2. Some products which were identified and are listed were present in too small a concentration to contribute to these chromatograms.

TABLE III
Products of the Catalyzed Degradation
of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

Compound	Relative abundance ^a	Means of identification ^b
N-Ethylaniline	major	RT, MS, B
Phenol	major	RT, A
N-Ethylskatole	minor	RT, MS, IR, PMR, N
N-Ethyl-N-methylaniline	minor	RT, MS, B
N,N-Diethylaniline	minor	RT, MS, B
N-Allyl-N-ethylaniline	minor	RT, MS, B
N-Ethyltetrahydroquinoline	minor	RT, MS, B
Phenetole	trace	RT, MS, N
Phenoxyacetone	trace	RT, MS, N
Chroman	trace	RT, MS, N
2-Methylbenzofuran } 3-Methylbenzofuran }	trace	RT, MS, N
2-Chromene	trace	RT, MS, N
N-Ethylindole	trace	RT, MS, N
1-Phenoxypropan-2-ol	trace	RT, N
3-Methyl-N-phenylpyrrole	trace	RT, MS, N
Benzofuran	trace	RT, MS, N
2-Methylcoumaran	trace	RT, MS, N
Phenyl vinyl ether	trace	RT, N
Anisole	trace	RT, N
3-Chromene	trace	RT, MS, N
Ethanol	trace	RT, MS, N
1-Propanol	trace	RT, MS, N
Acetaldehyde	trace	RT, N
Toluene	trace	RT, N
Acetone	trace	RT, N
Ethylbenzene	trace	RT, N
Styrene	trace	RT, N

^a The relative abundance of products was obtained by an estimation of the relative peak areas in the GLC chromatogram. The relative sensitivity of the flame ionization detector to individual compounds was not measured.

^b RT = GLC retention time; MS = mass spectrum; B = basicity; A = acidity; N = neutrality.

TABLE IV
 Products of the Uncatalyzed Degradation
 of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

Compound	Relative abundance	Means of identification
Phenol	major	RT, A
N-Ethyl-N-methylaniline	major	RT, MS, B
N-Ethylaniline	major	RT, MS, B
3-Methyl-N-phenylpyrrole	minor	MS, IR, PMR, N
N-Allyl-N-ethylaniline	minor	RT, MS, B
Benzofuran	minor	RT, MS, N
Benzaldehyde	minor	RT, N
2-Methylbenzofuran } 3-Methylbenzofuran }	minor	RT, N
<i>o</i> -Allylphenol	trace	RT, A
Anisole	trace	RT, MS, N
N-Ethylskatole	trace	RT, N
N,N-Dimethylaniline	trace	RT, MS, B
Ethylbenzene	trace	RT, MS, N
Toluene	trace	RT, MS, N
Benzene	trace	RT, N
Styrene	trace	RT, MS, N
N-Ethyltetrahydroquinoline	trace	RT, B
N-Ethylindole	trace	RT, N
Chroman	trace	RT, N
2-Chromene	trace	RT, N
Benzyl alcohol	trace	RT, N
3-Chromene	trace	RT, N
Acetone	trace	RT, N
Acetaldehyde	trace	RT, N
Phenetole	trace	RT, MS, N

DISCUSSION

Degradation Mechanisms

The uncatalyzed degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol gave rise to a large number of lower molecular weight products which, except for trace amounts of acetone and acetaldehyde, did not retain the oxygen function on the central aliphatic carbon atom. The nature of the products indicates that major reactions involve the scission of aliphatic carbon-oxygen bonds, the carbon-nitrogen bond, and the carbon-carbon bond adjacent to nitrogen. Phenol, N-ethylaniline, and N-ethyl-N-methylaniline are the major products; those resulting from scission of the aliphatic carbon-carbon bond adjacent to the phenoxy group occur in minor quantities. The diversity of the products suggests that radical processes are involved in their formation. The reaction and rearrangement of free radicals produced by homolytic scission of the aliphatic bonds in the starting material can be used to explain¹⁰ the formation of the degradation products. There are, however, many possible routes to the

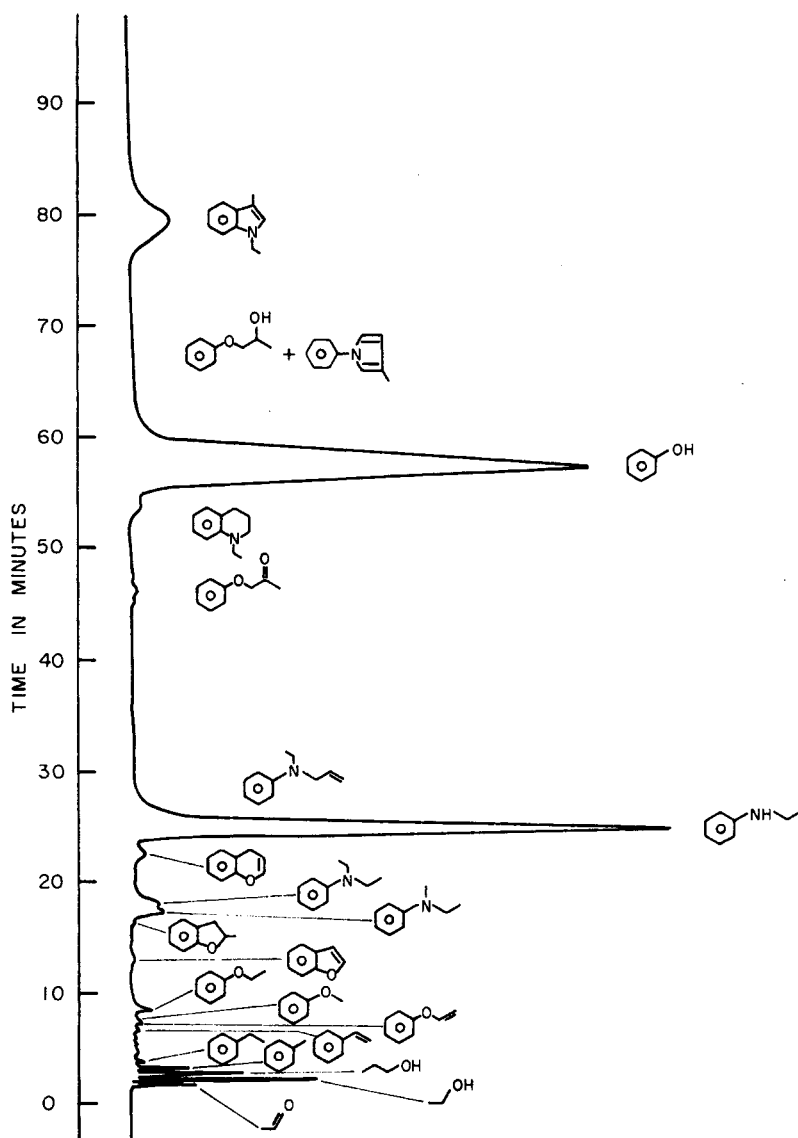


Fig. 1. GLC trace of the products of the catalyzed degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

formation of several products, and it is at this stage premature to propose detailed degradation mechanisms.

Accurate data for the bond dissociation energies of 1-(N-ethylanilino)-3-phenoxypropan-2-ol are not available. Since the aliphatic bonds have approximately the same standard bond dissociation energies,¹² there is no apparent reason for the preferential fission of only three of these bonds in the degradation. However, a possible explanation for such fissions to give

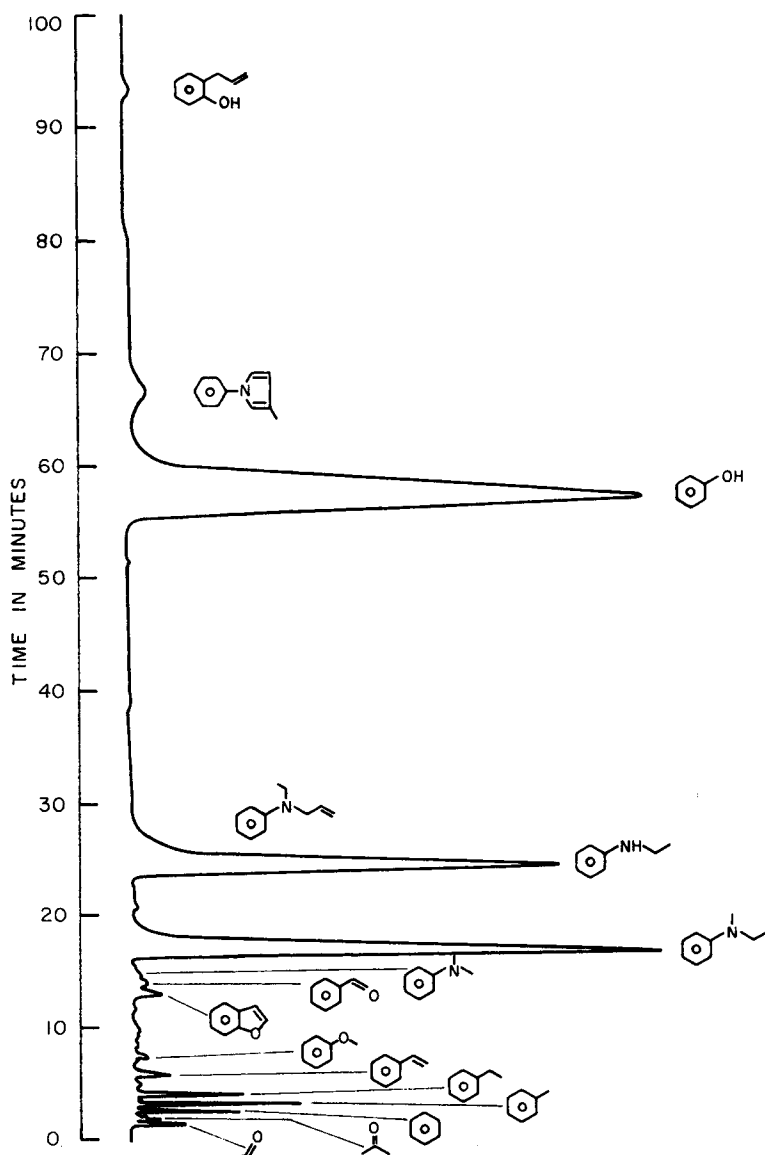


Fig. 2. GLC trace of the products of the uncatalyzed degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

the major products phenol, N-ethylaniline, and N-ethyl-N-methylaniline follows.

The nitrogen atom, by virtue of its lone pair of electrons, may promote base-catalyzed dehydration reactions. Dehydration of the starting material would give rise to the four isomeric 1-(N-ethylanilino)-3-phenoxypropenes (Fig. 3) containing allyl-nitrogen or allyl-oxygen bonds which have low bond dissociation energies.¹² Scission of these bonds would lead

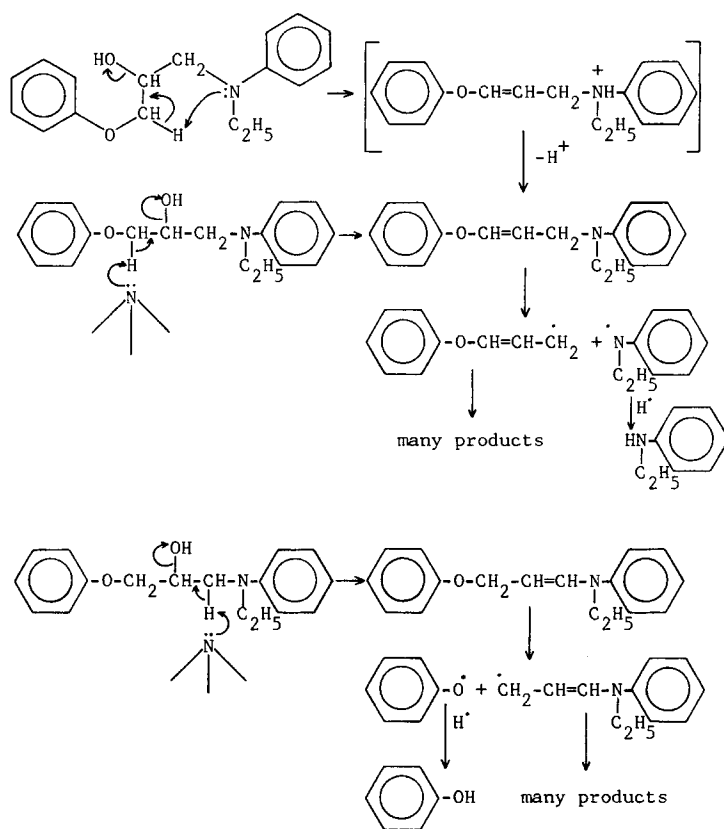


Fig. 3. Dehydration products of 1-(N-ethyl-anilino)-3-phenoxypropan-2-ol.

to the formation of phenol and N-ethyl-aniline. The bond dissociation energy of the single carbon-carbon bond in allyl groups is high.¹² The formation of N-ethyl-N-methylaniline with the possibly concurrent formation of benzofuran from the dehydrated structures is not feasible. N-Ethyl-N-methylaniline may be produced by the mechanism outlined in Figure 4, which involves a nucleophilic attack by the nitrogen atom on a γ -hydrogen atom analogous with the intramolecular dehydration in Figure 3.

The nature of the products of the catalyzed degradation of 1-(N-ethyl-anilino)-3-phenoxypropan-2-ol indicates that fission has occurred predominantly at the aliphatic carbon-oxygen and carbon-nitrogen bonds giving rise to phenol and N-ethyl-aniline as the major products. The production of smaller amounts of N-ethyl-N-methylaniline and N,N-diethylaniline indicates that aliphatic carbon-carbon bond fission has also occurred. In contrast with the uncatalyzed degradation, significant amounts of products representing hydrogen addition rather than dehydration reactions (phenetole and N,N-diethylaniline) are formed, and only a small quantity of N-ethyl-N-methylaniline is produced. This suggests

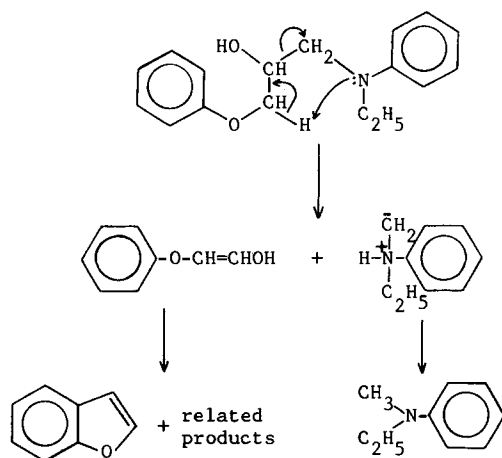


Fig. 4. A possible route to N-ethyl-N-methylaniline.

that in the catalyzed degradation, the alumina actually inhibits reactions in which the nitrogen atom plays a specific role in the uncatalyzed degradation. It is known^{13,14} that the nitrogen atom, like the oxygen atom, reacts with alumina.

The Effect of Alumina on the Degradation of Amine-Cured Epoxy Resins

The catalytic effect of alumina on the degradation of the model compound has been demonstrated. It is clear that the incorporation into an epoxy resin of fillers which have catalytic properties such as alumina and silica flour may greatly affect its performance at elevated temperatures.

The Mechanism of the Thermal Degradation of Bisphenol A-Based Epoxy Resins

The major products (phenols, N,N-dimethylanilines, N-methylanilines, and benzofuryl structures) of the low-temperature (300°C) degradation⁷ of the *p,p'*-diaminodiphenylmethane-cured diglycidyl ether of bisphenol A are similar in structure to the major products of the degradation of the model compound. Products resulting from fission of the aliphatic carbon-carbon bond adjacent to the phenoxy group are not observed.⁷ The production of large amounts of water (65% of the total possible water production⁷) in the degradation of aromatic amine-cured epoxy resins as well as the presence of double-bond structures in degraded resins^{1,5,6} provide evidence for dehydration reactions occurring in the degradation of these resins. The presence of resonance-stabilized free radicals in degraded epoxy resins^{3,5} provides evidence for free-radical mechanisms being involved in their degradation.

The results of the present study are in line with the results of previous studies of the thermal degradation of amine-cured epoxy resins. There

is evidence to suggest that degradation of the cure linkage involves homolytic scission of aliphatic bonds and that dehydration and a specific reaction to form methylanilino and benzofuryl structures, such as that depicted in Figure 4, possibly precede degradation to a large extent.

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References

1. D. P. Bishop and D. A. Smith, *Ind. Eng. Chem., Int. Ed.*, **58**, 32 (1967).
2. L. H. Lee, *J. Polym. Sci. A*, **3**, 859 (1965).
3. M. A. Keenan and D. A. Smith, *J. Appl. Polym. Sci.*, **11**, 1009 (1967).
4. J. M. Stuart and D. A. Smith, *J. Appl. Polym. Sci.*, **9**, 3195 (1965).
5. D. A. Smith, *Amer. Chem. Soc., Div. Org. Coat. Plast., Chem. Preprints*, **27**, 321 (1967).
6. J. C. Paterson-Jones and D. A. Smith, *J. Appl. Polym. Sci.*, **12**, 1601 (1968).
7. E. C. Leisegang, A. M. Stephen, and J. C. Paterson-Jones, *J. Appl. Polym. Sci.*, **14**, 1961 (1970).
8. D. P. Bishop and D. A. Smith, *J. Appl. Polym. Sci.*, **14**, 205 (1970).
9. D. O. Bowen, *Mod. Plast.*, 127 (1967).
10. V. A. Percy, M.Sc. Thesis, University of Cape Town, South Africa, December 1971.
11. Y. M. Beasley, V. Petrow, and O. Stephenson, *J. Pharm. Pharmacol.*, **10**, 47 (1958).
12. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, vol. 1, translated by J. E. S. Bradley, Pergamon Press, New York, 1958, p. 16.
13. J. B. Peri, *J. Phys. Chem.*, **69**, 231 (1965).
14. J. M. Parera and N. S. Figoli, *J. Catal.*, **14**, 303 (1969).

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