A radiochemical study of the kinetics of epoxide cure: Reaction of phenyl glycidyl ether and other model epoxides with various imidazoles

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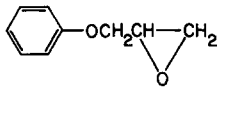
The reactions of phenyl glycidyl ether and other model epoxides with a series of imidazoles have been investigated using a new radiochemical procedure. In the case of phenyl glycidyl ether and imidazoles containing a free imino group, there is an initial induction period that is a function of both the polarity of the medium and the reaction temperature. This reaction exhibits a first-order dependence on imidazole concentration (< 0.2 M) but at higher values the rate becomes independent of imidazole concentration. These features are also observed for several other epoxides. Evidence is presented to show that the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole is catalysed by the 1:1 complex formed and also by 1,3-bisphenoxypropan-2-ol, propan-2-ol and phenol, in that order of effectiveness. The effect on reaction rates of structural alterations to both the epoxides and the imidazoles is also discussed.

(Keywords: epoxide cure; imidazoles; tritiated compounds; radio high-performance liquid chromatography; phenyl glycidyl ether)

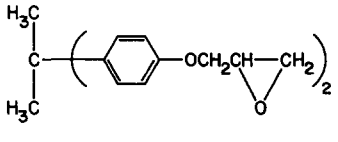
INTRODUCTION

In recent years there has been a great increase in the number of applications of epoxy resins, especially in the field of high-performance composite materials. This has been accompanied by an increasing activity in the investigation of the process of resin network formation or cure[1]. However, the mechanisms of reaction of epoxy resins with curing agents are still far from being fully understood, partly because of the complexity of the reactions and partly because of the lack of precise methods for monitoring them. Two of the most widely used techniques are Fourier transform infra-red spectroscopy[2], and differential scanning calorimetry[3]; the former relies on spectral changes and the latter on enthalpy differences, so that both are somewhat restricted in terms of reactions that can be studied and the information that they can provide.

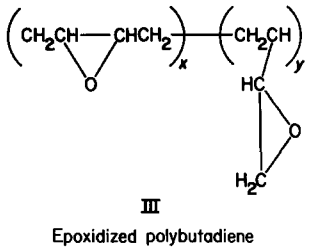
One very interesting group of curing agents for epoxy resins is imidazole and its derivatives, but there have been relatively few reported investigations into the reactions of these compounds with epoxides[4-9]. In the present study we partly rectify the situation by studying the reaction between phenyl glycidyl ether (I) and a series of imidazoles. The former was chosen because it bears a close resemblance to the diglycidyl ether of bisphenol-A (II), the most widely used commercial epoxide, whilst the latter are known to produce resins with good high-temperature properties. There are, however, other types of epoxides, e.g. aliphatic epoxides such as epoxidized polybutadiene (III), cycloaliphatic epoxides such as vinylcyclohexene dioxide (IV), glycidyl amines such as diglycidylphenylamine (V), and aliphatic glycidyl ethers such as the diglycidyl ether of ethanediol (VI), that are used commercially. It seemed appropriate, therefore, that, in order to study the effect of epoxide structure on



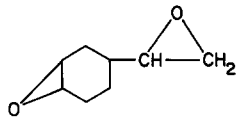
I
Phenyl glycidyl ether



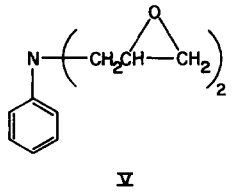
II
Bisphenol-A diglycidyl ether



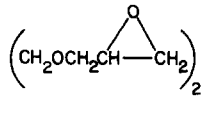
III
Epoxidized polybutadiene



IV
Vinylcyclohexene dioxide



V
Diglycidylphenylamine



VI
Ethanediol diglycidyl ether

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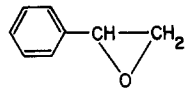
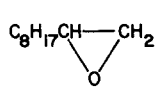
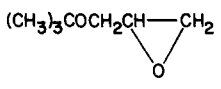


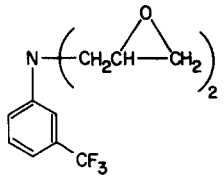
VII
Styrene oxide



VIII
1,2-Epoxydecane



IX
t-Butyl glycidyl ether



X
(*m*-Trifluoromethylphenyl) diglycidylamine

the kinetics of the curing reaction, model epoxides VII–X, representative of these classes, be chosen to react with imidazole itself.

In the majority of industrial applications, epoxy resins are used as solventless systems, that is, cure is carried out as a bulk reaction in which the curing agent is merely dissolved in the epoxide. It was therefore decided to study the kinetics under similar conditions, and in order to establish an experimental procedure that could be made applicable to a large number of systems we developed a radiochemical method. This entailed labelling the imidazoles with tritium, using a one-step catalytic procedure, and determining the pattern of labelling using ^{3}H n.m.r. spectroscopy[10]. (These details are the subject of a separate publication[11].) The tritiated imidazole was then reacted with a known epoxide and at selected time intervals samples were withdrawn, quenched and separated using high-performance liquid chromatography. The decrease in the radioactivity of the midazole as well as the appearance of radioactivity in the product(s) could then be used to follow the kinetics of the reaction(s). These details together with the results obtained are the subject of the present publication; some related information has recently been published[12].

EXPERIMENTAL

Materials

With the exception of (*m*-trifluoromethylphenyl-) diglycidylamine, which was kindly provided by Dr P. Johncock (RAE), all the other epoxides were commercially available. In all cases their purity was checked prior to use. Similarly, with the exception of those detailed below, the imidazoles were purchased from commercial sources.

Substituted 4,5-diphenylimidazoles (numbers 5, 6, 7, 8 and 9 in *Table 3*) were prepared using the method of Davidson *et al.*[13] Benzil (1,2-diphenylethanedione) (0.01 moles), ammonium acetate (0.1 moles) and the appropriate substrate (0.01 moles) were refluxed in glacial acetic acid (100 ml) for 1 h. The reaction mixture was cooled to room temperature and poured into iced water (500 ml), whereupon the imidazole was precipitated. Recrystallization was effected from a 1:1 ethanol–water solution.

2-(*p*-Dimethylaminophenyl)-4,5-dimethylimidazole was prepared by refluxing butane-2,3-dione (0.9 g), *p*-dimethylaminobenzaldehyde (1.5 g) and ammonium acetate (7.0 g) in glacial acetic acid (100 ml) for 2 h. The resulting solution was poured into water (500 ml) to give a dark red solution. The crude product, together with some unreacted aldehyde, was precipitated from solution by the addition of an excess of sodium carbonate. The precipitate was collected and the crude imidazole separated from the aldehyde by dissolving the mixture in 0.5% acetic acid solution. This solution was gravity filtered to remove the aldehyde and excess sodium carbonate added to the filtrate to precipitate the imidazole. Further purification was effected by recrystallization from a 1:1 ethanol–water solution.

The 1:1 adduct of phenyl glycidyl ether and 2-ethyl-4-methylimidazole was prepared by adding to a stirred, refluxing solution of 2-ethyl-4-methylimidazole (27.5 g) in toluene (200 ml), over the course of 1 h, a solution of phenyl glycidyl ether (37.5 g) in toluene (50 ml). The mixture was refluxed for a further 2 h and on cooling the product precipitated; after separation and washing with ether it was further purified by column chromatography using a silica stationary phase and 4:1 chloroform–methanol as the eluant.

Kinetic procedure

The tritiated imidazole was diluted with inactive compound to bring the specific activity down to the range required for radio h.p.l.c. analysis. A known quantity (of the order of a few milligrams) was then added to the epoxide (2 ml) in a round-bottomed flask maintained in a thermostat at the required temperature. Known amounts (50 μl) of the reaction mixture were withdrawn at fixed time intervals and the reaction quenched by dilution and cooling with cold acetone (1 ml). The reaction mixture was separated into its components by injecting samples (20 μl) onto a column (12 cm stainless steel packed with Spherisorb ODS5 (5 μm porous silica spheres coated with a C_{18} alkyl)) and eluted using isocratic mixtures of acetonitrile, acetic acid and water containing 0.1% of the sodium salt of pentanesulphonic acid. The eluant was mixed in a 1:3 ratio with liquid scintillant (NE 260, Nuclear Enterprises) and the resulting solution passed through the Isoflo 1 radioactivity detector, where the various tritiated compounds can be detected. The electrical output of the Isoflo 1 was transmitted to an Apple IIe computer, which analysed the signal and displayed the variation of radioactivity (in counts per second) with time.

Analysis of kinetic data

The radio h.p.l.c. results show how the imidazole concentration as represented by its radioactivity decreases with time and how new products (the 1:1 and 2:1 adducts can be readily identified by comparison with the retention times of synthesized products) are formed. The present investigation was concerned solely with the first complex-forming step and, as the concentration of the tritiated imidazole was much smaller than the epoxide, first-order kinetics were observed; k_{obs} was therefore obtained from the slope ($-k_{obs}/2.303$) of the plot of $\log_{10}(C_t - C_\infty)$ against time, C_t being the radioactivity of the imidazole at different times and C_∞ the corresponding value (effectively zero) at the end of the reaction.

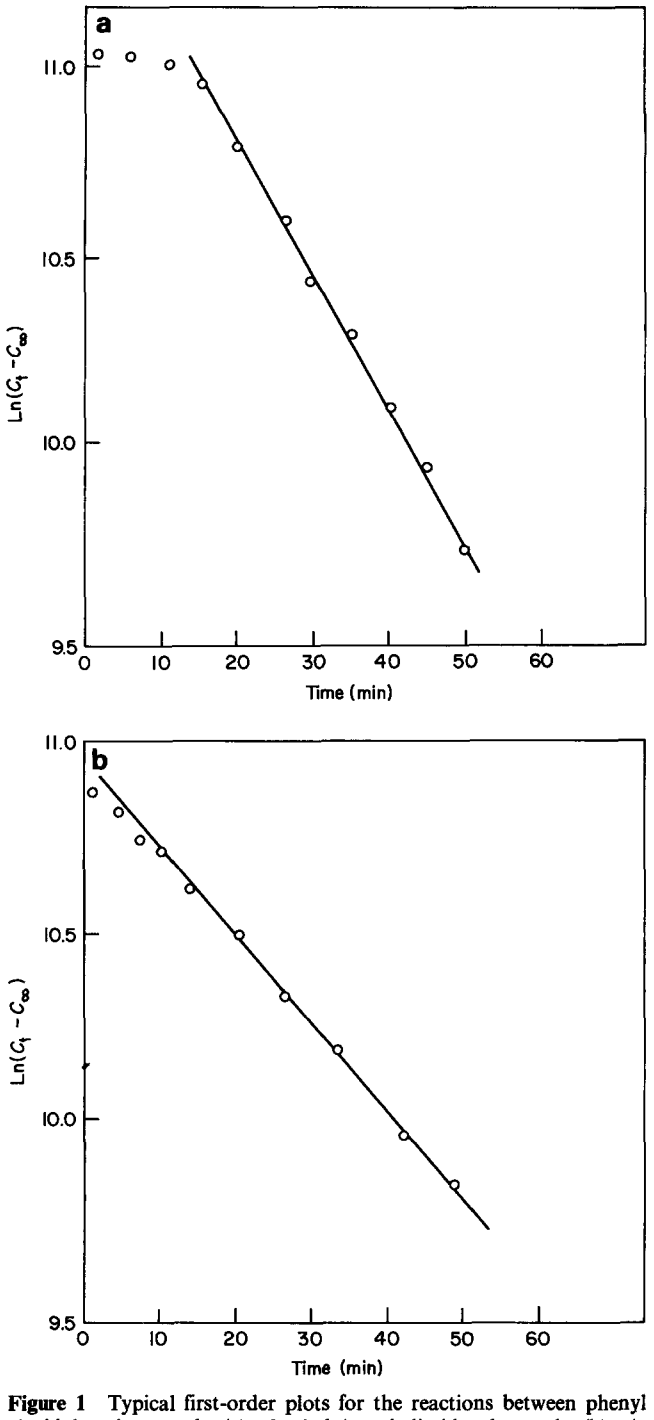
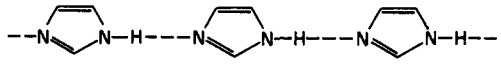


Figure 1 Typical first-order plots for the reactions between phenyl glycidyl ether and (a) 2-ethyl-4-methylimidazole and (b) 1-methylimidazole, at 85°C

RESULTS AND DISCUSSION

The first-order plots (*Figure 1a*) for the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole are characterized by an initial induction period, which is typically of the order of 10–20 min at 85°C, becoming shorter at higher temperatures. In contrast, the plots for the corresponding 1-substituted imidazoles, e.g. 1-methylimidazole (*Figure 1b*), are strictly linear. Ethers commonly have low dielectric constants (< 20) and this is the most probable reason for the difference, as under these circumstances the 1-unsubstituted imidazoles will tend to associate in the following manner:



something that the 1-substituted imidazoles will not be able to do. Independent evidence supporting this viewpoint is available. Thus when the molecular weights of imidazoles are determined by cryoscopic or ebulliometric methods in non-polar solvents, large deviations from ideal behaviour are observed, e.g. for 4-methylimidazole in benzene the apparent molecular weight[14] is almost 20 times the expected value. Similarly, the apparent dipole moment of imidazole in benzene varies considerably with concentration, whereas that of 1-methylimidazole remains constant[15]. This interpretation was reinforced by an experiment in which propylene carbonate ($\varepsilon = 66.1$ at 20°C) was added to the reaction medium, with the result that the induction period vanished.

For the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole over the temperature range 75–95°C, the dependence of the observed rate constant k_{obs} on imidazole concentration is as shown in *Table 1*. The data at 80°C are plotted in *Figure 2*, from which it is seen that up to about 0.2 M the reaction is strictly first-order with respect to imidazole concentration but gradually reduces to lower values at higher concentrations. Indeed, at the highest temperature, the reaction is effectively zero-order and this behaviour is observed for several 1-unsubstituted imidazoles (*Table 3*) at 95°C. Interestingly for several 1-substituted imidazoles at this temperature, and higher, the reaction remains first-order at the lower concentrations, thus enabling the second-order rate constants k_2 ($=k_{obs}/[Im]$) to be calculated (*Table 2*). Clearly the effectiveness of the imidazoles increases in the order 2-ethyl-4-methyl > 1-methyl > 1-benzyl-2-methyl ≃ 1,2-dimethyl.

The kinetic data for the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole and also 1-methylimidazole when plotted in terms of an Arrhenius equation give linear relationships from which the following values were derived: $E_{act} = 202 \pm 18$ kJ mol^{-1}, log $A = 29.3 \pm 2.8$ for the former; and $E_{act} = 187 \pm 23$ kJ mol^{-1}, log $A = 26.6 \pm 3.4$ for the latter.

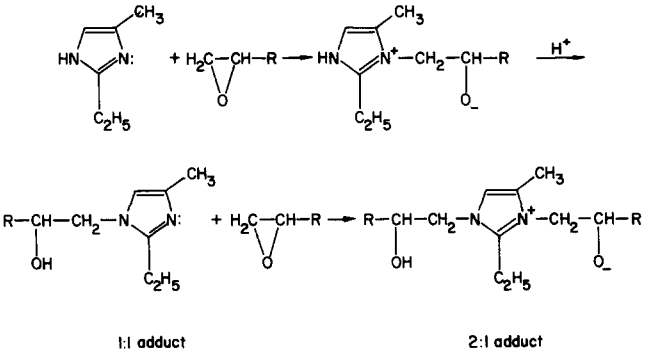
For the reaction between phenyl glycidyl ether and a number of 1-unsubstituted imidazoles at 95°C (*Table 3*) for which a zero-order dependence on imidazole concentration is observed, if we assume that the k_2 values

Table 1 First-order rate constants k_{obs} (min^{-1}) for the reaction of phenyl glycidyl ether and 2-ethyl-4-methylimidazole at different temperatures

[Im] (M)	$10^2 k_{obs}$ (min^{-1})				
	75°C	80°C	85°C	90°C	95°C
0.02	0.25	0.50	1.52	4.89	
0.025	0.32	0.63			
0.050	0.65	1.5	3.5	10.1	50.0
0.10		1.9	9.1	16.0	
0.15		3.5			
0.20	2.1	4.6	11.1	24.9	50.5
0.40			16.0		
0.55		8.0			
0.80		10.3			
1.0		12.0			
1.16	8.0	13.0	23.7	35.2	50.7

were to parallel the k_{obs} values then the differences are readily understandable in terms of electronic effects. The inclusion of electron-donating groups, including a phenyl group in the C-2 position, increases the rate of adduct formation whilst electron-withdrawing groups, including phenyl at positions 4 and 5, decrease the rate. This trend is shown most clearly in the results for the 2,4,5-triphenylimidazoles. The insertion of a *p*-nitro group on the 2-phenyl group would be expected to cause a decrease in the reactivity of the imidazole by removal of electron density from the tertiary nitrogen through resonance effects whilst the converse is true for the *p*-dimethylamino group. Although the *o*-methoxy group is inductively electron-withdrawing, it is mesomerically electron-donating and, as is often the case, this mesomeric effect is greater than the inductive effect. The sum total effect of the structural alterations was to produce a compound, 2-(*p*-dimethylaminophenyl)-4,5-dimethylimidazole, which was even more effective than 2-ethyl-4-methylimidazole in the curing reaction.

The observed substituent effects taken together with the generally observed first-order rate dependence on imidazole concentration are consistent with the now accepted mechanism[4,6] for the first few stages of epoxide cure. This consists of nucleophilic attack by the tertiary nitrogen of the imidazole on the epoxide ring, leading to a zwitterion, which then rearranges by proton transfer to give the 1:1 adduct, which itself reacts with a second molecule of epoxide to form the 2:1 adduct, thus:



The effect of the 1:1 adduct on the rate of the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole was investigated at 80°C. At low concentrations the reaction was first-order in adduct concentration, and *Table 2* shows that the derived second-order rate constant k_2 is some 6 times greater than for 2-ethyl-4-methylimidazole. This could mean an inherent difference in reactivity; it could also mean that attack on the epoxide takes place via the hydroxyl group as well as the tertiary nitrogen. That this is a possibility is illustrated by the effect that adding various alcohols to the reaction medium has on the rate (*Figure 3*): 1,3-bis-phenoxypropan-2-ol is more effective than propan-2-ol or phenol but less so than the 1:1 adduct.

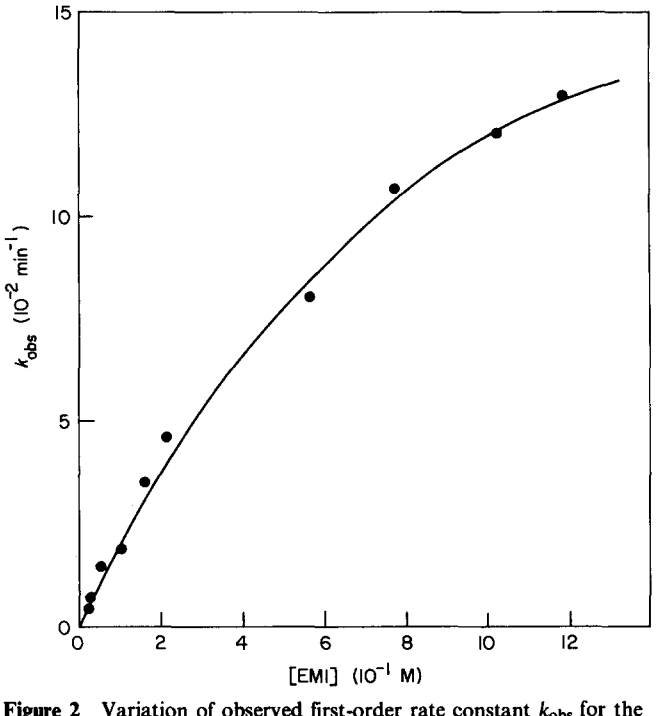


Figure 2 Variation of observed first-order rate constant k_{obs} for the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole at 80°C

Table 3 Observed first-order rate constants k_{obs} (min^{-1}) at 95°C for the reaction between phenyl glycidyl ether and various imidazoles[a]

	Imidazole	$10^2 k_{obs}$ (min^{-1})
1.	Imidazole	35
2.	2-Ethyl-4-methylimidazole	50
3.	2-Phenylimidazole	55
4.	2-Methylimidazole	44
5.	4,5-Diphenylimidazole	4.2
6.	2,4,5-Triphenylimidazole	6.2
7.	2-(*p*-Nitrophenyl)-4,5-diphenylimidazole	3.0
8.	2-(*O*-Methoxyphenyl)-4,5-diphenylimidazole	8.3
9.	2-(*p*-Dimethylaminophenyl)-4,5-diphenylimidazole	13
10.	2-(*p*-Dimethylaminophenyl)-4,5-dimethylimidazole	85

[a] Under the experimental conditions, the rates are independent of imidazole concentration

Table 2 Second-order rate constants k_2 (M^{-1} min^{-1}) for the reaction of phenyl glycidyl ether and various imidazoles at different temperatures

	k_2 (M^{-1} min^{-1})					
Imidazole	75°C	80°C	85°C	90°C	95°C	105°C
2-Ethyl-4-methylimidazole	0.13	0.25	0.73	2.25		
1-Methylimidazole		0.056	0.27		1.37	4.3
1-Benzyl-2-methylimidazole					0.072	
1,2-Dimethylimidazole					0.069	
1:1 Adduct of phenyl glycidyl ether and 2-ethyl-4-methylimidazole		1.6				

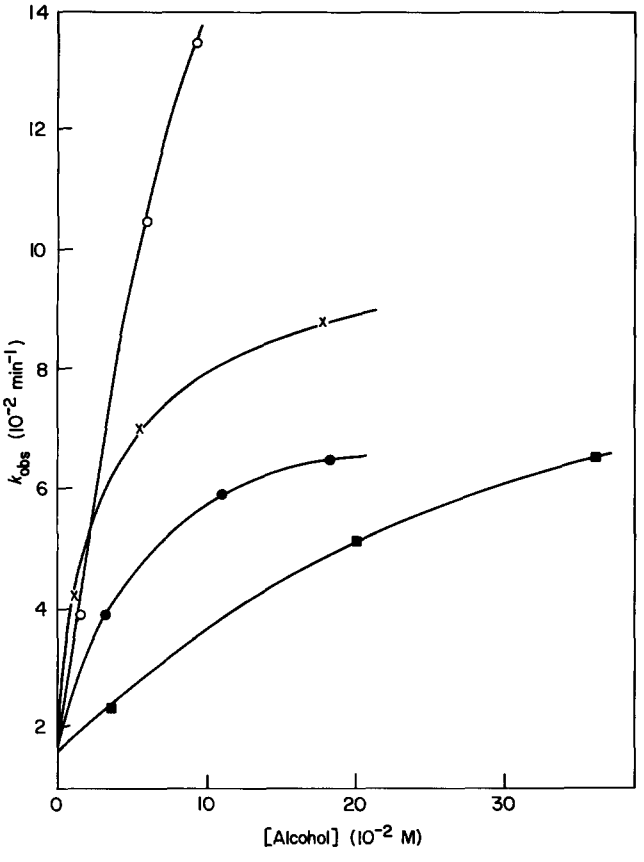


Figure 3 Variation of observed first-order rate constant k_{obs} for the reaction between phenyl glycidyl ether and 2-ethyl-4-methylimidazole at 80°C in the presence of added alcohols: ○, 1:1 adduct; ×, 1,3-bisphenoxypropan-2-ol; ●, propan-2-ol; ■, phenol

Table 4 Second-order rate constants k_2 (M^{-1} min^{-1}) at 95°C for the reaction of various model epoxides with imidazole

Epoxide	k_2 (M^{-1} min^{-1})
Styrene oxide (VII)	0.46
1,2-Epoxydecane (VIII)	0.30
t-Butyl glycidyl ether (IX)	0.48
(*m*-Trifluoromethylphenyl) diglycidylamine (X)	1.5

When other epoxides were investigated, similar features to those observed for phenyl glycidyl ether were witnessed. Thus with imidazole itself compounds VII and X all gave an induction period, its duration decreasing with increasing imidazole concentration. The reactions were all first-order in imidazole concentration (< 0.1 M) with the exception of 1,1,1-trichloropropene oxide, which was strictly zero-order. The derived second-order rate constants (*Table 4*) are closely similar, suggesting that structural alterations in the epoxide have less of an effect on the rate than do changes in the imidazole structure, although a true comparison would have to relate the data to a single solvent system.

Finally, the observations that for two epoxides a zero-order dependence on imidazole concentration was witnessed and that for phenyl glycidyl ether at 95°C some nine additional imidazoles (not substituted at N-1) behaved similarly, suggest that the explanation lies not in a change of mechanism but rather in associated effects similar to those responsible for the observed induction periods.

ACKNOWLEDGEMENT

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