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LUIGI STANDOLI, STEFANO CORSANO

**The kinetic effect of epoxy group in the alkaline  
hydrolysis of glycidic esters**

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**Chimica organica.** — *The kinetic effect of epoxy group in the alkaline hydrolysis of glycidic esters.* Nota di LUIGI STANDOLI e STEFANO CORSANO, presentata (\*) dal Socio L. PANIZZI.

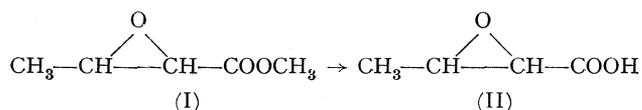
RIASSUNTO. — È stato messo in evidenza mediante misure cinetiche che il gruppo  $\alpha,\beta$  epossidico produce un effetto accelerante sulla idrolisi degli esteri.

Tale effetto è stato attribuito, anche sulla base di misure di  $pK_a$ , ad una stabilizzazione per risonanza dell'intermedio formatosi durante il processo di idrolisi alcalina.

While the reactions of oxirane toward nucleophilic agents have been well studied [8], minor attention has been paid to the effect of  $\alpha,\beta$  epoxy group in nucleophilic reactivity of neighbouring groups [7].

During the reduction of glycidic esters and lactones by sodium boron hydride, one of us has observed a strong accelerating effect produced by the epoxy group on the reaction rate [5].

In order to require more information on the accelerating effect produced by the epoxy-group we have extended our researches to the alkaline hydrolysis of glycidic ester(I).



We have first of all checked the behaviour of ester(I) in the experimental conditions used for the kinetic determinations and we have found that the only product formed is the glycidic acid(II). We have also observed that the rate of hydrolysis of (I) follows a second order kinetic and the results are shown in Table I.

TABLE I

*Rate constants for the alkaline hydrolysis of some butyrate esters in 50% methanol at 25°.*

Compound	T °C	$10^2 k_2 \text{ l. mol}^{-1} \text{ sec}^{-1}$	$k/k_0$
Methyl 2,3 epoxy butyrate (a) (I) . . .	25	131 (b)	107
Methyl 2 hydroxy butyrate (c) (III) . .	25	15.2 (d)	12.4
Methyl 2 methoxy butyrate (e) (IV) . .	25	2.3 (f)	1.9
Methyl butyrate (V) . . . . .	25	1.22 (g)	1

(a) Ref. [4], (b) Std. dev. 0.03; Corr. coeff. 0.991; (c) Ref. [3]; (d) Std. dev. 0.01 Corr. coeff. 0.998; (e) Ref. [2]; (f) Std. dev. 0.02; Corr. coeff. 0.996; (g) Std. dev. 0.016; Corr. coeff. 0.998.

(\*) Nella seduta del 12 aprile 1975.

The comparison with the rate constants for the hydrolysis of methyl butyrate and of some  $\alpha$ -substituted esters, confirms this interesting accelerating effect produced by the  $\alpha,\beta$ -epoxy group during the nucleophilic attack on the ester group.

In order to ascertain at what extent the enhancement of the rate may be attributed to the inductive and field effects, we have also determined the pKa of glycidic acid(II), which showed (Table II) a value smaller than that of butyric acid(VI), but slightly higher to that of 2-hydroxy butyric acid(VII).

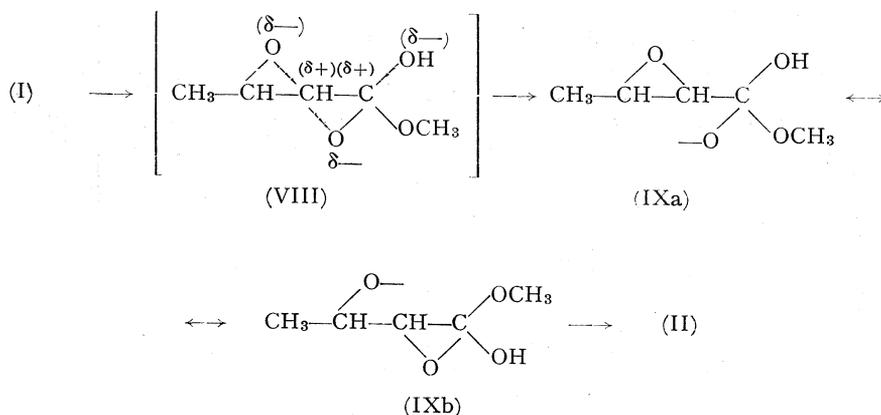
Clearly, glycidic acid(II) appears to be a stronger acid, however(II) is slightly less acidic than 2-hydroxy butyric acid(VII); since (I) is nearly 10 times more reactive than (III) other factors beside the inductive and field effects seem to be responsible of the acceleration observed in the hydrolysis reaction.

TABLE II  
*Ionization constants of acids.*

Compound	pKa
2-3 epoxy butyric acid (II) . . . . .	3.94 <sup>(a)</sup>
<i>n</i> butyric acid (VI) . . . . .	4.82 <sup>(b)</sup>
2 hydroxy butyric acid (VII) . . . . .	3.81 <sup>(b)</sup>

(a) This work; mean dev. 0.02. Average of 4 determination;  
(b) Ref. [1].

We suggest, as hypothesis, that the accelerating effect of  $\alpha,\beta$  epoxy group can be due to a stabilization of the tetrahedral intermediate as described in the resonating structure VIII a and VIII b, whose structure showed be very similar to the activated complex, with corresponding lowering of the energy of activation of the process.



Similar accelerating effect will be shown also, probably, by cyano and carbonyl compounds conjugated with an epoxy group.

#### EXPERIMENTAL

*Materials.* The preparation of compounds used was carried out by the method previously described in the literature [2, 3, 4].

The methyl 2,3 epoxy butyrate(I) was not known and were prepared by esterification with  $\text{CH}_2\text{N}_2$  of acid. (b.p. 86-87/50 mm.) The infrared and n.m.r. spectra were consistent with the assigned structure).

*Kinetic measurement.* Equal quantities of 0.01 N solution of esters and sodium hydroxide in 50% methanol (by weight) which had attained thermal equilibrium in the thermostat, were mixed.

Five-ml. samples were removed of the appropriate amounts of time and pipetted in a known excess of dilute hydrochloric acid.

Titration of this mixture was affected to a phenolphthalein end-point using standard sodium hydroxide solution.

*Measurement of pKa.* Samples of each acid (ca.  $10^{-2}$  mol) were dissolved in ethanol-water (1 : 1); the titration flask at 25° in a water bath was purged with nitrogen and the acid solution was titrated with 0,2 N sodium hydroxide. A Radiometer model 26 pH meter with standard glass and calomel electrodes was employed.

The pKa values were calculated from the Henderson equation [6] and are the average of three determinations at ca. 20,40 and 60% of neutralization.

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