BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3651—3652 (1970)

Thermal Decarboxylation of Nitrobenzoic Acids. I

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(Received November 12, 1969)

Thermal decarboxylation of *o*-, *m*- and *p*-nitro benzoic acids was studied in glycerol in the temperature range 210—250°C *m*- and *p*-Nitrobenzoic acids exhibited first order rate constants and in support of the proposed S_E1 mechanism, the isomers were also studied in aniline at 110—140°C. Pseudo-first order rate constants of the ortho isomer in glycerol suggested a change in mechanism from S_E1 to S_E2. The rate constants were influenced by boric acid or aniline added to glycerol as the result of a change in pH and confirmed thus the proposed S_E1 or S_E2 mechanisms. Activation energies, enthalpies and entropies of activation were obtained for the three isomers.

A survey of literature of several organic acids reveals that decarboxylation occurs either by unimolecular or bimolecular electrophilic substitutions, S_E1 or S_E2.[1] The S_E1 mechanism requires the loosening of R–C bond, and the substituents which diminish the electron density on the α-carbon atom facilitate this mechanism as in the cases of nitro acetic, nitro-isobutyric,[2] trihaloacetic[3] and cyanoacetic acids.[4]

The view that decarboxylation by S_E2 mechanism involves the attack of a proton or a protonated solvent on the α-carbon atom of the carboxyl group is supported by Schenkel and Schenkel-Rudin,[5] Hammick and coworkers[6] and Muhammad and Siddiqui.[7] A polyhydric alcohol glycerol was used as a solvent in the studies of decarboxylation of hydroxy benzoic and chlorobenzoic acids and 1-hydroxy-2-naphthoic acid.[8]

In view of the above studies, the decarboxylation of *o*-, *m*- and *p*-nitrobenzoic acids was carried out in the solvents glycerol and aniline in order to study their mechanisms.

Results and Discussion

***m*- and *p*-Nitrobenzoic Acids.** Decarboxylation of the *m*- and *p*-nitrobenzoic acids in the solvents glycerol and aniline is kinetically first order. The rates, being faster in the basic solvent aniline than in glycerol, suggest that these isomers follow the unimolecular S_E1 mechanism. The rate constants and the other thermodynamic parameters are shown in Table 1.

Substances such as aniline and boric acid added to glycerol alter the acidity of the medium and the rate constants, as in Table 2 (a) and (b), also exhibit a marked increase and decrease for the meta and para isomers respectively in support of the S_E1 mechanism. The stability of the two isomers in the acidic solvent, resorcinol is an additional support for the proposed mechanism.

The presence of a nitro group either in the meta or para position in benzoic acid, by withdrawing electrons, deactivates the ring and facilitates the C–C bond cleavage. Glycerol being a polyhydric alcohol ionizes the acids to a less extent than aniline.

A comparison of the rates, enthalpies and entropies of activation reveals that a more basic solvent aniline favours the S_E1 mechanism rather than a neutral solvent glycerol, and is in good agreement with the observation of Clark.[9a] In these solvents it has been visualised that the electrophilic carbon

TABLE 1. THERMODYNAMIC PARAMETERS FOR DECARBOXYLATION IN GLYCEROL AND ANILINE

	Solvent: Glycerol, Temp.: 200—250°C					Solvent: Aniline, Temp.: 100—150°C			
Acid	pK_a	$k \times 10^4$ 230° sec^{-1}	$\Delta E^{\neq}$ kcal·mol^{-1}	$\Delta H^{\neq}$ kcal·mol^{-1}	$\Delta S^{\neq}$ e.u.	$k \times 10^3$ 130° sec^{-1}	$\Delta E^{\neq}$ kcal·mol^{-1}	$\Delta H^{\neq}$ kcal·mol^{-1}	$\Delta S^{\neq}$ e.u.
o-NO_2	2.17	6.26	35.10	34.10	− 6.04	—	—	—	—
m-NO_2	3.46	11.66	17.31	16.31	−40.95	1.25	26.15	25.22	−9.59
p-NO_2	3.43	11.39	17.30	16.30	−41.02	2.33	30.52	29.59	+2.43

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Table 2. Effect of added substances on decarboxylation in glycerol

a) *m*-Nitrobenzoic acid at temp. 214°C		b) *p*-Nitrobenzoic acid at temp. 230°C	
Amount of aniline added	$k\times10^4$ sec^{-1}	Amount of Boric acid added	$k\times10^4$ sec^{-1}
0%	7.35	0%	12.01
0.4%	13.96	1%	10.75
0.8%	16.58	2%	7.60
1.4%	18.32	8%	2.63

Table 3. Effect of added boric acid in the decarboxylation of *o*-nitrobenzoic acid in solvent glycerol at temperature 235°C

Amount of boric acid added	pH	$k\times10^4$ sec^{-1}
0%	7.20	8.90
0.5%	3.07	11.89
1.0%	3.02	15.26
1.5%	2.97	18.01
2.0%	2.94	21.95

atom of an undissociated acid apparently co-ordinates with an unshared pair of electrons on a nucleophilic atom of the polar solvent favouring the subsequent cleavage of the molecule into the products.[9b)]

Since the rate determining step involves the decomposition of the transition state, the extent of formation of this state depends on the polarizability of the carboxyl carbon atom as well as on the nucelophilicity of the solvent. Therefore, it can be suggested that the greater the availability of the electrons on the neucleophilic atom of the solvent, the greater would be the probability of the formation of the activated state. Hence, in the activated state, the nucleophilic aniline interacts more readily than glycerol with the carbon atom of the carboxyl group resulting in high enthalpies and entropies of activation. However, as the accepting ability of the carbon atom of the carboxyl group does not change much in the two isomers, it is the basicity of the solvent that plays an important role in the formation of the transition stage. The rate constants, activation energies and other thermodynamic parameters are nearly the same in the weakly basic solvent glycerol comparable to their pK_a value. But in the highly basic solvent aniline, the effective electrophilicity developed on the α-carbon atom of the carboxyl group in the two isomers also plays a role and shows an increase in the thermodynamic parameters, similar to the change from glycerol to aniline.

o-Nitrobenzoic Acid. The kinetics of decarboxylation of *o*-nitrobenzoic acid in glycerol follows a different pattern from that of the other two isomers. The rate of ortho acid (Table 1) is small compared to its meta and para isomers and exhibit pseudo-first order rate constants. The rate constants also show an increase with added boric acid to glycerol as the result of a change in pH (Table 3).

It was also observed that the ortho isomer decarboxylates more easily in acidic solvent, resorcinol, and is stable in basic solvent, aniline, unlike the meta and para isomers. This exhibits a change in mechanism from S_E1 to S_E2 since the latter are acid-catalyzed.

It has been suggested that the geometry of the ortho-transition state of *o*-nitrobenzoate ion exhibits a dipolar interaction of the type as in Fig. 1, the stereochemistry of the transition state being suitable for the electrophilic substitution. This type of internal chelation[10)] is mainly responsible for a change in mechanism and the decarboxylation proceeds in the anionic form.

$$k = [\mathrm{RCOO^-}][\mathrm{H^+}]$$

Fig. 1

Besides the chelation in the case of ortho isomer, deactivating influence of nitro group in ortho position will be less. This is due to the fact that the nitro group, which is in the same plane as the benzene in para isomer, deactivates the carbon atom mostly due to resonance interaction. However, in ortho position, because of steric effect, the nitro group is twisted out of the plane of benzene ring. Hence, the resonance inter-action will become less, and deactivating influence will be diminished compared to its para or meta isomer.

Experimental

The experimental procedure and the calculation of the rate constants were similar to the one adopted in 1-hydroxy-2-naphthoic acid.[8)] The experiments were carried out with B.D.H. and analar samples of ortho, meta and para nitrobenzoic acids and the solvents glycerol and aniline were of pure quality, which did not emit any carbon dioxide when heated alone. In all the experiments, the final volume of carbon dioxide was calculated theoretically. The kinetics were followed in all cases, till 25—30% of acid was decarboxylated. The reactions were studied in the temperature range 200—250°C in glycerol and 110—135°C in anilline.

The authors wish to thank Professor N.V. Subbarao for his keen interest and one of the authors (D.S.) is grateful to the Government of India for the Award of a Research Training Scholarship.

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