Effect of Metal Ions on the Radiation-Induced Decarboxylation of Aqueous Benzoic and Salicylic Acid Solutions

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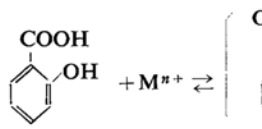
Remarkable effect of heavy metal ions was observed in the radiolysis of benzene in aqueous solution[1] and other organic compounds[2]. In the systems hitherto studied, the interaction between metal ions and organic molecules is expected to be different from that in the compounds containing metal ions. The effect of metal ions bound to organic molecules on the radiolysis has not yet been studied.

The present authors studied the effects of added ions on the decarboxylation of benzoic and salicylic acids, in order to clarify the difference in the effect between bound and non-bound metal ions. Benzoic acid does not form any chelate compounds with metal ions, whereas salicylic acid gives stable complexes with Fe^{3+}, Cu^{2+} and Al^{3+}.



(1)

The difference in the effect of heavy metal ions on $G(CO_2)$ was found between benzoic and salicylic acid, and this can be attributed to the difference in the states of ions.

The oxygen free solution containing 0.2 % of either acid and metal salts were irradiated by ^{60}Co γ-rays in the test tube with side cell in which 0.1 N barium hydroxide solution was

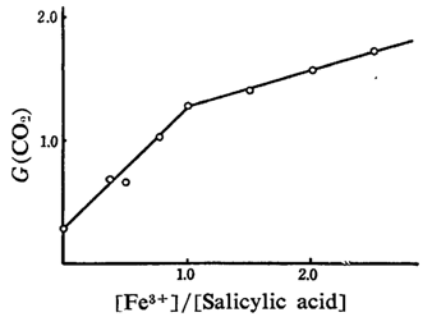


Fig. 1. The effect of Fe^{3+} concentration on $G(CO_2)$ of salicylic acid.

1) J. H. Baxendale and D. Smithies., *J. Chem. Phys.*, 23, 604 (1955); *J. Chem. Soc.*, 1959, 779.
2) E. A. Cherniak, E. Collinson, F. S. Dainton and G. M. Meaburn, *Proc. Chem. Soc.*, 1958, 54.

TABLE I. EFFECTS OF SALTS ADDED ON $G(CO_2)$

Acid	Salt added		$G(CO_2)$
Salicylic acid		—	0.29
	$FeCl_3$	1.4 mol.	1.38
	$FeSO_4$	1.4 mol.	0.27
	$CuCl_2$	1.4 mol.	0.47
	$AlCl_3$	1.4 mol.	0.26
	$CoCl_2$	1.4 mol.	0.23
	$NiCl_2$	1.4 mol.	0.26
	$ZnCl_2$	1.4 mol.	0.28
	$MgCl_2$	1.4 mol.	0.28
	H_2SO_4	(0.8 N)	0.55
	H_2SO_4 (0.8 N) $FeCl_3$	1.4 mol.	0.65
	KF $FeCl_3$	8.3 mol. 1.4 mol.	0.11
Benzoic acid		—	0.66
	$FeCl_3$ pH~1	2.8 mol.	0.30

placed in order to absorb carbon dioxide formed. Dose rate and total dose were 9.5×10^4 r./hr. and 1.57×10^6 r., respectively. Carbon dioxide formed was absorbed by barium hydroxide solution and $G(CO_2)$ was measured volumetrically.

The effects of various metal ions are summarized in Table I. In the case of benzoic acid, Fe^{3+} added does not bring about the increase in $G(CO_2)$, while in the case of salicylic acid, it makes $G(CO_2)$ remarkably high. This suggests that Fe^{3+}, chelating organic molecules and attacking redicals cooperate in the decarboxylation of the complex. This is also supported by the following experiments.

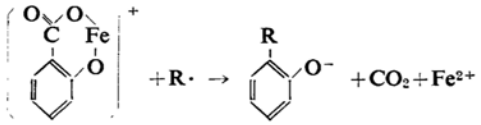
a) Fig. 1 shows the plot of $G(CO_2)$ in the radiolysis of salicylic acid against the amount of Fe^{3+} added. As is shown in the figure, a remarkable break is observed at $[Fe^{3+}]/[\text{Salicylic acid}]=1$, where all of Fe^{3+} ions and salicylic acid mulecules exist as complexes and neither of Fe^{3+} nor salicylic acid remains in excess.

b) The addition of some masking reagents such as F^- and H^+ to the complex makes $G(CO_2)$ low.

Based on the above results, the mechanism of the decarboxylation of the complexes is conceivably different from that of free acids.

Therefore the following sequence of reactions can be given for the decarboxylation of the complex.

$$H_2O \xrightarrow{\gamma\text{-rays}} H\cdot + HO\cdot + H_2O_2 \quad \text{etc.} \tag{2}$$



(3)

(where R· represents free radical)

The attacking radical (R·) is not yet identified but this mechanism is supported by the following observations.

a) In this case Fe^{3+} is easily reduced to Fe^{2+}, although it is reduced only to small extent in the absence of organic compounds.

b) Fe^{3+} and Cu^{2+} added bring about the increase in $G(CO_2)$ of salicylic acid, whereas added Al^{3+} has only a slight effect. All of them are known as metal ions which give complexes with salicylic acid.

These indicate that both the complex formation and easy reduction of metal ions are essential for this kind of metal catalyzed radiation-induced decarboxylation.

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