Carbon and Oxygen Isotope Effects in the Decarbonylation of Benzoylformic Acid in Concentrated Sulphuric Acid

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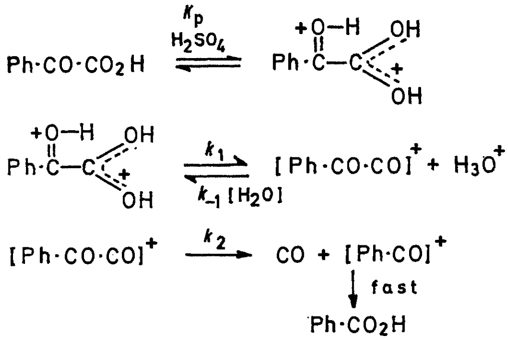
Summary Kinetic isotope effects for carbon and oxygen for the decarbonylation of benzoylformic acid in concentrated sulphuric acid have been measured, which, together with measurements on isotopic exchange of oxygen with the solvent, support a mechanism in which C–O bond rupture occurs in the rate-determining step.

DECARBONYLATION, or loss of carbon monoxide, of carboxylic acids in concentrated sulphuric acid occurs in a group of acids which includes oxalic, formic, and benzoylformic acids. A mechanism of the reaction for these acids was first suggested by Hammett.[1] In the case of benzoylformic acid the reaction is:



SCHEME 1

A study of both the carbon and oxygen isotope effects of the atoms involved in the reaction can provide evidence for this mechanism. Since the oxygen of the bond cleaved yields water which is immediately absorbed by the solvent, sulphuric acid, it is not possible to measure the change in the isotopic composition of oxygen in the primary product (water) directly. Therefore, new kinetic equations were derived for calculating the oxygen isotope effect from the oxygen remaining in the carbon monoxide.[2]

TABLE 1

Oxygen-18 isotope effects			Carbon-13 isotope effects	
Intermolecular	Intramolecular	Secondary	Carboxyl carbon	Carbonyl carbon
$2k_3/k_1$	k_3/k_2	$2k_2/k_1$	k_{13}/k_{12}	k_{13}/k_{12}
0·981 ± 0·002	0·986 ± 0·001	0·995 ± 0·001	0·947 ± 0·001	1·000 ± 0·001

The intra- and inter-molecular isotope effects[3] are then given by:

(a) The *intramolecular* oxygen isotope effect is the ratio of the rate constants for bond cleavage to ^{16}O (k_2) and to ^{18}O (k_3) in the same molecule.

$$(C^{16}O/C^{18}O)_{t\to\infty} = (M_1{}^0/M_2{}^0)(1 - k_3/k_2)$$

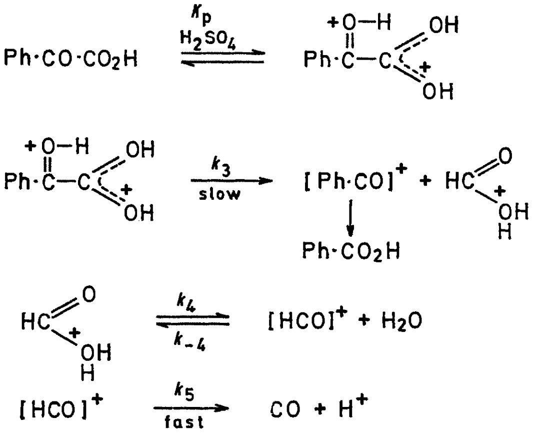
where $M_1{}^0/M_2{}^0$ is the initial ratio of $^{16}O/^{18}O$ in the acid.

(b) The *intermolecular* oxygen isotope effect is the ratio of the rate constants for bond cleavage to ^{16}O and to ^{18}O in two different molecules:

$$k_3/k_1 = [(C^{16}O/C^{18}O)_{t\to\infty} - (M_1{}^0/M_2{}^0)]/(C^{16}O/C^{18}O)_{t\to 0}$$

where k_1 is the rate constant for bond cleavage in an all ^{16}O molecule and k_3 as before.

Both carbon and oxygen isotope effects for decarbonylation of benzoylformic acid in 99·8% H_2SO_4 at 0° were determined by analysing the starting materials and products for their isotopic composition. Samples were measured as either carbon monoxide or carbon dioxide in an Atlas M86 mass spectrometer against standards using the δ system.[4] The results are given in Table 1, where k_{12} and k_{13} are the rate constants for breaking bonds to ^{12}C and to ^{13}C respectively.



SCHEME 2

As part of his studies on the decarbonylation of formic acids, Ropp[5] measured the ^{14}C isotope effect of the *carbonyl* carbon in benzoylformic acid and found a value of 3·9%. This is inconsistent with the mechanism outlined in Scheme 1.

To account for this unusually large isotope effect for an atom not directly involved in bond breaking, an alternative scheme can be suggested in which C–C bond rupture is the rate-limiting step.

A kinetic analysis was made[2] for each of these mechanisms. In addition to the decarbonylation reaction, isotopic exchange of oxygen between the carboxyl group and the water in the solvent can occur. This exchange is expressed by reversible reactions with rate constants k_1 and k_{-1} in Scheme 1 and k_4 and k_{-4} in Scheme 2.

Using the rate and equilibrium constants indicated above, equations can be derived for the observed rate of decarbonylation, as follows:—

$$\text{Scheme 1: } k_{\text{exp}} = k_1k_2/(k_{-1}[\text{H}_2\text{O}] + k_2) \times K_p h_0^2$$

$$\text{Scheme 2: } k_{\text{exp}} = k_3K_p h_0^2$$

where h_0 is the Hammett acidity function. An analysis of these equations indicates that when C–O bond rupture is the rate-limiting step (Scheme 1), an isotope effect of the carbon carbonyl can be observed, only when there is isotopic exchange of oxygen with the medium, since k_{exp} is a function of k_{-1} (the rate constant for the incorporation of oxygen from the solvent) and of k_2 (the rate constant for C–C bond rupture). It was shown there should be no carbon isotope effect when there is no isotopic exchange, since when k_{-1} is negligible, k_{exp} is a function of k_1 only. On the other hand, these calculations show that when C–C bond rupture is the rate-determining step (Scheme 2) there should be a carbon isotope effect of the carbonyl carbon atom under all conditions (see Table 2), since in this case k_{exp} is proportional to k_3 (the rate constant for C–C bond rupture).

Contrary to previous reports[5] it was found that isotopic exchange of oxygen does occur between benzoylformic acid and ^{18}O-enriched sulphuric acid, the rate depending on the acid concentration. However, in 99·5—100° H_2SO_4 at 0°, no exchange could be observed during decarbonylation, for which reason the measurements were made under these conditions.

TABLE 2

	Type of bond rupture	Oxygen exchange with medium	Carbon isotope effect of the carbonyl carbon atom: *predicted*	Carbon isotope effect of the carbonyl carbon atom: *found*
Scheme 1	C–O	yes	yes	yes
Scheme 2	C–C	yes	yes	
Scheme 1	C–O	no	no	no
Scheme 2	C–C	no	yes	

The experimental and the predicted results for the isotope effect of the carbonyl *carbon* atom are summarized in Table 2. The experimental results, *i.e.* that a carbon isotope effect occurs when there is exchange[5] and none when there is no exchange (Table 1) show unequivocally that the rate-limiting step in >99% H_2SO_4 is C–O bond rupture, and that the Hammett mechanism is correct. These results indicate that in the use of isotope effects in complex organic reactions, a detailed kinetic analysis of all the steps involved, including isotopic exchange is essential.

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