

748. *Mechanism of Decarbonylation. The Kinetics of the Decarbonylation of Benzoylformic Acid in Slightly Aqueous Sulphuric Acid.*

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The decarbonylation of (loss of carbon monoxide from) benzoylformic acid in slightly aqueous sulphuric acid has been found to be a first-order process, and the variation of rate constant with temperature to be expressed by the equation $k = 9.4 \times 10^{10} \cdot e^{-18,800/RT}$ sec.⁻¹. The rate of reaction is markedly inhibited by the addition of basic solutes, and the variation of reaction rate with the concentration of inhibitor may be accounted for by assuming that decarbonylation proceeds by unimolecular decomposition of the benzoylformic diacidium ion, $C_6H_5 \cdot C \begin{array}{l} \parallel \\ \text{OH} \end{array} - C \begin{array}{l} \text{OH} \\ \parallel \\ \text{OH} \end{array} \text{OH}^+$, and that this unstable

ion is only formed to a limited extent in the solvent, sulphuric acid 98% plus water 2%.

THE decarbonylation reaction, *i.e.*, the degradative reaction whereby a carbonyl group is eliminated from an organic compound as carbon monoxide, occurs in a wide variety of types of carbonyl compound, *e.g.*, α -keto-acids, α -hydroxy-acids, formic and oxalic acids and their derivatives, aldehydes, ketones, and acids of the type $R_3C \cdot CO_2H$, where R may be an alkyl or an aryl group. The reaction occurs under a variety of conditions, *e.g.*, pyrolysis, proton-acid catalysis, Lewis-acid catalysis, base catalysis. There has been, however, relatively little work reported on the mechanism of the reaction. The kinetics of decarbonylation of formic acid (Schierz, *J. Amer. Chem. Soc.*, 1923, **45**, 447; De Right, *ibid.*, 1933, **55**, 4761), citric acid (Wiig, *ibid.*, 1930, **52**, 4729), oxalic acid (Lichty, *J. Phys. Chem.*, 1907, **11**, 225), malic acid (Whitford, *J. Amer. Chem. Soc.*, 1925, **47**, 953; Dittmar, *ibid.*, 1930, **52**, 2747), and triphenylacetic acid (Dittmar, *ibid.*, 1929, **51**, 533) have been studied in sulphuric acid solutions, but no satisfactory mechanism of reaction has been suggested by the above workers. Decarbonylation of ethyl pyruvate (Calvin and Lemmon, *ibid.*, 1947, **69**, 1232) and diphenylpropane-1 : 2 : 3-trione (dibenzoylformaldehyde) (Roberts, Smith, and Lee, *ibid.*, 1951, **73**, 618) has been studied

by using radioactive tracers. Calvin and Lemmon (*loc. cit.*) showed that, in the case of ethyl pyruvate, the carboxyl-carbon atom is eliminated as carbon monoxide.

We have investigated the decarbonylation of benzoylformic acid in slightly aqueous sulphuric acid: $\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H} \longrightarrow \text{Ph}\cdot\text{CO}_2\text{H} + \text{CO}$. This acid was chosen since (a) the decarbonylation had been reported to be quantitative (Bistrzycki and Siemiradzki, *Ber.*, 1906, **39**, 51), (b) there is little change in the acidity of the solution as the reaction proceeds, and (c) the acid contains no basic groups other than those requisite to the reaction and contains no labile hydrogen atoms.

EXPERIMENTAL.

The decarbonylation was followed kinetically by measuring the volume of carbon monoxide evolved at constant pressure. The apparatus is represented diagrammatically in Fig. 1. A known volume of mercury is let out of the gas burette into the flow-meter (*F*), and the time take to restore atmospheric pressure in the gas burette is indicated by the mercury in the manometer arm (*M*) making a contact which causes a bell to ring. A further volume of mercury is let out and the process repeated until the run is complete. By this simple means it is possible to follow a fast rate of gas evolution closely and accurately. This method is especially suitable for studying gas evolutions that take place rapidly at or near room temperature, where there is little or no variable temperature gradient in the apparatus.

Each experimental run was commenced by melting the benzoylformic acid in the reaction tube, supercooling it to room temperature, and adding the solvent. A mercury-sealed stirrer was then fitted and, after some 10 minutes' stirring to allow thermal equilibrium to be established, readings were commenced. Temperature control to within 0.02° was ensured by an electrically heated water-bath.

In certain cases the rate constant was determined from the rate of formation of benzoic acid. This was found by titration, the benzoic acid being removed from the reaction mixture by diluting a sample with water and extracting the acid with carbon disulphide.

Results.

That the reaction is a normal homogeneous reaction in solution has been demonstrated in two ways. First, the rate of evolution of carbon monoxide was found to be independent of the nature of the walls of the reaction vessel if the reaction mixture was stirred. Secondly, the rate of formation of benzoic acid in the absence of stirring is the same as the rate of evolution of gas when the reaction mixture is stirred.

The rate of evolution of carbon monoxide was found to be a first-order process with respect to benzoylformic acid. Details of a specimen kinetic run are given below, and the rate of gas evolution, volume against time, is plotted in Fig. 2.

Volume units	0	2	4	6	8	10	12	14	16	18
Time, sec.	0	18	38	61	84	112	140	170	204	240
Volume units	20	22	23	24	25	26	27	28	28.5	29
Time, sec.	284	336	368	406	448	491	544	606	650	693

Temperature 306.0°K . Solvent, 98% H_2SO_4 in large excess.

The rate constant was determined from Fig. 2 by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538). The $\log(v' - v)$ terms are tabulated below and, from the plot against time, it is found that the slope = $0.434k = 0.00151$; *i.e.*, $k = 0.00344 \text{ sec.}^{-1}$.

Time, sec.	0	40	80	120	160	200	240	280	320
v_T	0	4.20	7.60	10.60	13.40	15.85	18.05	19.85	21.35
v'_{T+360}	22.80	23.80	24.80	25.75	26.60	27.25	27.90	28.40	28.85
$\log(v' - v)$	1.358	1.292	1.235	1.180	1.121	1.057	0.993	0.932	0.875

Though most of the rate constants were calculated by this method, a few runs were allowed to go to completion, and in such cases the rate constants calculated by the end-volume method agree with those calculated by Guggenheim's method.

The rate constants observed at various temperatures are tabulated below. The variation of rate constant with temperature may be expressed by the equation

$$k = 9.4 \times 10^{10} \cdot e^{-18,800/RT} \text{ sec.}^{-1}$$

Temp., $^\circ \text{K}$	291.3	297.9	302.3	306.0
$10^4 k$, mean, obs.	7.14	14.6	25.0	34.3
$10^4 k$, calc.	7.25	14.8	23.5	34.7

These results were obtained with a mixture containing 98% (by weight) sulphuric acid and 2% water as solvent, which was in large excess over the solute, benzoylformic acid. This concentration of sulphuric acid was used so that the concentration of bisulphate ions present in the excess of solvent should be large compared with that of bisulphate ions arising from the ionisation of the benzoylformic acid according to the equilibrium

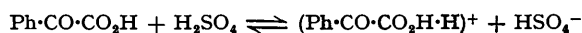


FIG. 1.

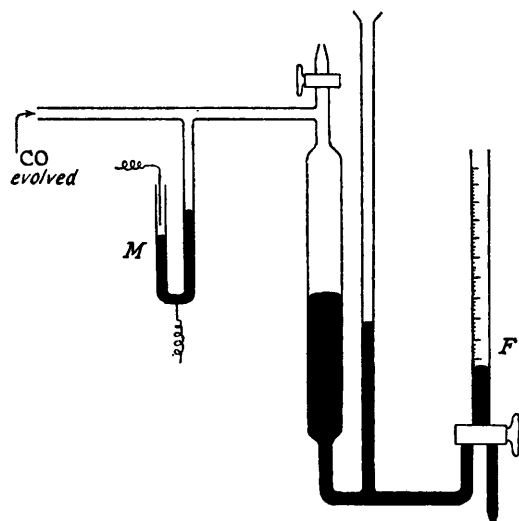


FIG. 2.

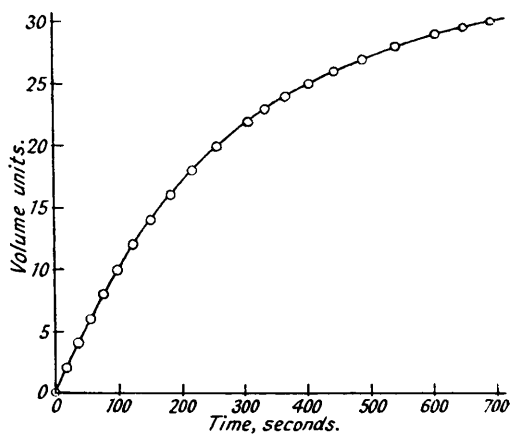
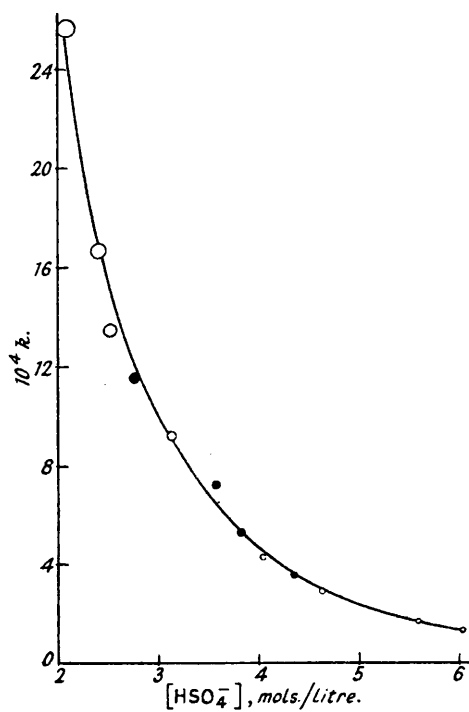
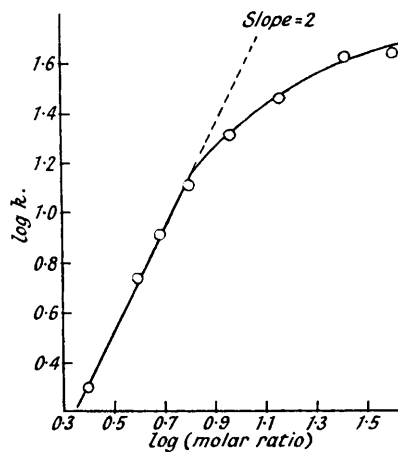


FIG. 3.



- HSO_4^- due to H_2O .
 ● HSO_4^- due to $\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$.

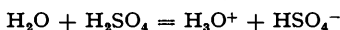
FIG. 4.



The variation of reaction rate by the addition of the solutes water and potassium sulphate was determined by making up solvents of various composition by direct weighing. Details are tabulated below and the rate constants are plotted against bisulphate-ion concentrations in Fig. 3.

Comptn. of solvent, % by wt. :			Molarities of solvent :			Comptn. of solvent, % by wt. :			Molarities of solvent :		
H ₂ SO ₄	H ₂ O	K ₂ SO ₄	Undiss. H ₂ SO ₄	HSO ₄ ⁻	10 ⁴ k, sec. ⁻¹	H ₂ SO ₄	H ₂ O	K ₂ SO ₄	Undiss. H ₂ SO ₄	HSO ₄ ⁻	10 ⁴ k, sec. ⁻¹
98.00	2.00	nil	16.24	2.03	25.0	94.43	5.57	—	11.97	5.64	1.77
97.63	2.37	—	15.80	2.40	16.7	94.05	5.95	—	11.49	6.02	1.37
97.53	2.47	—	15.67	2.51	13.5	94.40	1.93	3.67	16.23	2.75	11.6
96.92	3.08	—	14.95	3.13	9.27	90.39	1.84	7.77	14.85	3.58	7.39
96.03	3.97	—	13.87	4.03	4.35	89.26	1.82	8.92	14.34	3.82	5.36
95.43	4.57	—	13.15	4.63	2.95	86.81	1.77	11.42	13.79	4.36	3.69

The molarities of undissociated sulphuric acid and of bisulphate ions have been calculated by assuming that the basic solutes react according to the equations :



In order to determine the molarities recorded above, the densities of the H₂SO₄-H₂O-K₂SO₄ mixtures were determined by the relative density method. The densities determined at 18° were corrected to the reaction temperature (29.1°) and are recorded below.

Comptn. of solvent, % by wt.				Relative density
H ₂ SO ₄	H ₂ O	K ₂ SO ₄		
98.00	2.00	—		1.827
95.07	1.94	2.99		1.848
90.70	1.85	7.45		1.880
86.36	1.76	11.88		1.912

From Fig. 3 it can be seen that the inhibition produced by the addition of the basic solutes is dependent on the concentration of the bisulphate ions produced by the basic solute; *e.g.*, the addition of 2 g.-mol./l. of water produces the same effect as the addition of 1 g.-mol./l. of potassium sulphate.

In order to indicate the order of the catalytic effect of the solvent, the rate of decarbonylation was determined under conditions where the solvent, 98% sulphuric acid, was not in large excess. This procedure virtually dilutes the solvent. An inert solvent cannot be employed as diluent since aprotic solvents are immiscible with sulphuric acid, and basic solvents, *e.g.*, nitrobenzene, inhibit the reaction. The observed rate constants and molar ratios of sulphuric acid to benzoylformic acid are tabulated below, and in Fig. 4 log (rate constant) is plotted against log (molar ratio).

Molar ratio	2.56	3.88	4.83	6.29	9.30	14.6	25.9	40.8
10 ⁴ k, sec. ⁻¹	1.93	5.50	8.10	12.8	20.7	28.4	41.6	40.6

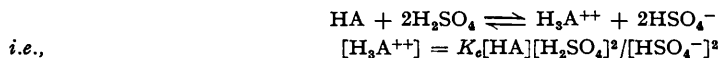
The decarbonylation of formic acid at 18.15° in 98% sulphuric acid was investigated and the rate constant found to be 42.8×10^{-4} sec.⁻¹. Under the same conditions the rate of decarbonylation of benzoylformic acid is 7.1×10^{-4} sec.⁻¹. Therefore the decomposition of benzoylformic acid is unlikely to involve a fast preliminary solvolysis followed by decarbonylation of formic acid. This conclusion is supported by the fact that the rate of formation of benzoic acid is equal to the rate of evolution of carbon monoxide.

Ethyl benzoylformate is not decarbonylated under conditions similar to those employed in the kinetic experiments upon benzoylformic acid. Gas evolution, however, commences at *ca.* 60° and benzoic acid is produced. It is thought likely that the ester is decarbonylated by means of a preliminary hydrolysis to benzoylformic acid, since both ethyl benzoylformate and ethyl benzoate are reasonably stable in 98% sulphuric acid at room temperature, but benzoic acid is produced in both cases when the esters are heated to 80° for some ten minutes.

DISCUSSION.

The marked inhibition produced by the addition of bases indicates that some acidic or positive species essential to the reaction mechanism is destroyed by the basic solute or by the basic product of the basic solute, namely, the bisulphate ion. The positively charged species likely to be present in a solution of benzoylformic acid in slightly aqueous sulphuric acid are the benzoylformic mono- and di-acidium ions, the ions derived from the autoprotolysis of the solvent, and hydroxonium ions. In order to ascertain the active species, the logarithm of the rate constant was plotted against Hammett and Deyrup's values for the acidity function H_0 (*J. Amer. Chem. Soc.*, 1932, 54, 2721). The slope of the plot was -2.1 , indicating that the reactive species may be the benzoylformic diacidium ion, *i.e.*, the product of the transfer of two protons from the solvent to the neutral substrate. In this connection it may be pointed out that both benzoic acid and acetone are strong bases in sulphuric acid (Gillespie, *J.*, 1950, 2473). If this conclusion is valid, it requires that the acidity function H_0 should vary

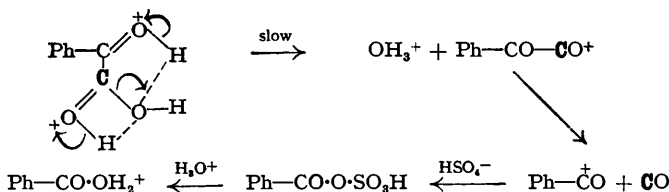
approximately as the acidity function H_+ over the investigated range of acidities, *i.e.*, $\Delta H_0 \simeq \Delta H_+$, where H_+ is the acidity function for a unit positively charged conjugate base. This would require that the function $f_{BH^{+2}}/f_B \cdot f_{BH_3^{++}}$ is approximately constant over the determined range of acidities. The same conclusion may be reached without recourse to Hammett's acidity function. Thus



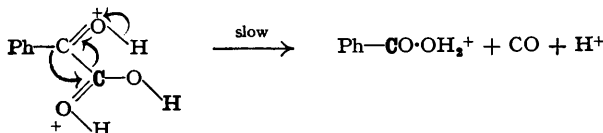
If the reaction rate is proportional to the concentration of the active species H_3A^{++} , then $[H_2SO_4]^2/[HSO_4^-]^2$ is proportional to the rate constant. The curve drawn in Fig. 3 is a plot of the function, constant $\times [H_2SO_4]^2/[HSO_4^-]^2$, and the excellent agreement obtained between this theoretically derived curve and the experimentally determined points indicates that the relation is obeyed. If this conclusion is valid it means that the activity coefficients may be ignored in the determined range of solvent concentrations. Gillespie (*loc. cit.*) has stated that interionic forces in sulphuric acid appear to be unusually low and that the cryoscopic constant may be calculated from the depression of freezing point produced by ionic solutes. Hammett and Lowenheim (*J. Amer. Chem. Soc.*, 1934, 56, 2620) have also found that ionic solutes appear to behave ideally up to ionic strengths of at least 2.

There appear to be two possible modes of decomposition of the benzoylformic diacidium ion :

(A) An interionic mechanism involving the loss of the carboxyl carbon atom as carbon monoxide :



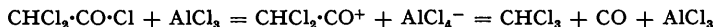
(B) An intramolecular rearrangement with the loss of the carbonyl carbon atom as carbon monoxide :



Mechanism (A) appears to be the more probable; for, first, Calvin and Lemmon (*loc. cit.*) have shown that the carboxyl carbon atom is lost in the pyrolytic decarbonylation of ethyl pyruvate, and secondly, there appears to be some evidence for the finite existence of an intermediate carbonium ion in other decarbonylation reactions, *e.g.*, triphenylacetic acid (Dittmar, *loc. cit.*) :



and the aluminium chloride-catalysed decarbonylation of dichloroacetyl chloride (Boeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 417) :

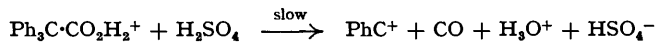


We have applied the foregoing methods to the experimental results of earlier workers, *i.e.*, plotting \log (rate constant) against H_0 and also against $\log [H_2SO_4]/[HSO_4^-]$, and the slopes thus found are tabulated below. Hammett (*Chem. Reviews*, 1935, 16, 67) has also plotted \log

Acid	Solvent range :		H_0 plot	$\log \frac{[H_2SO_4]}{[HSO_4^-]}$ plot
	H_2SO_4 , %			
Formic (De Right)	96 —98.5		1.2	1.2
Malic (Whitford)	96.5—99.2		ca. 0.9	1.1
Oxalic (Lichty)	90 —96		ca. 1.2	1.1
	98 —100		2.0	—
Citric (Wiig)	95 —98.8		ca. 2.0	2.1
Benzoylformic (present authors)	94 —98		2.1	2.0
Triphenylacetic (Dittmar)	93 —97		2.6	2.3

(rate constant) against H_0 and found approximately similar slopes to those here recorded, for formic, malic, citric, and triphenylacetic acids.

It would therefore appear that formic and malic acids decompose through their monoacidium ions and that citric and benzoylformic acids decompose through their diacidium ions in the solvent ranges indicated; also that oxalic acid may decompose through both types of ion, the di-acidium ion only existing in significant concentration in the solvent range 97—100% H₂SO₄. Triphenylacetic acid appears to be anomalous in two respects: first, it is the only case where the slopes are not approximately integral, and secondly, it is the only case where the number of protons taken up is apparently greater than the number of basic centres in the molecule. This would suggest that triphenylacetic acid decomposes by a different mechanism, perhaps by conversion into a monoacidium ion which interacts with the solvent without proton transfer, *e.g.*, a pseudo-unimolecular dehydration:



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