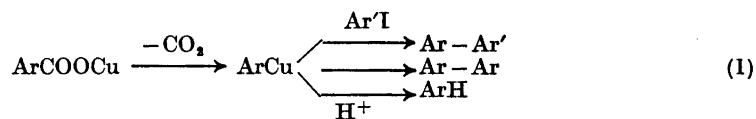# Kinetics of the Decarboxylation of Copper(I)

Nitrobenzoates in Quinoline

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The rates of decarboxylation of copper(I) 2-nitrobenzoate and copper(I) 4-nitrobenzoate in quinoline solution were measured in the temperature ranges $120-160°$ and $180-230°$, respectively. The reactions were pseudo first order until 85 % completion. Enthalpies and entropies of activation were calculated: for copper(I) 2-nitrobenzoate, $\Delta H^{\neq} = 20$ kcal mol^{-1}; $\Delta S^{\neq} = -26$ cal deg^{-1} mol^{-1}; for 4-nitrobenzoate $\Delta H^{\neq} = 17$ kcal mol^{-1}; $\Delta S^{\neq} = -40$ cal deg^{-1} mol^{-1}. The large negative entropies of activation indicate that several degrees of freedom are lost in the activated complex for decarboxylation. The activated complex thus probably involves a highly ordered structure, which also includes solvent participation.

Evidence is accumulating that copper-catalyzed decarboxylation of certain aromatic acids proceeds from the copper(I) salts of the acids through intermediate arylcopper compounds.[1-5] The latter may react further in various ways (eqn. 1).

$$\text{ArCOOCu} \xrightarrow{-CO_2} \text{ArCu} \begin{cases} \xrightarrow{\text{Ar'I}} \text{Ar} - \text{Ar'} \\ \xrightarrow{} \text{Ar} - \text{Ar} \\ \xrightarrow{\text{H}^+} \text{ArH} \end{cases} \tag{1}$$

In some decarboxylations the organocopper compounds may accumulate.[2] For nitrobenzoic acids [1,2] the further reactions of the assumed organocopper intermediate seem to be rapid and the direct verification of the assumed intermediate is more difficult to obtain. It is therefore of interest to study the primary process in decarboxylation. We have measured the carbon dioxide evolution from the copper(I) salts of 2-nitrobenzoic and 4-nitrobenzoic acids in quinoline solution. In these reactions no trapping agent for the presumed organocopper intermediate was present. The further reactions were therefore uncontrolled. Particularly the formation of metallic copper in further reactions could influence the results. As shown in eqn. 1 copper-catalyzed decarboxyla-

tion has several applications.[1-5] The further study of the mechanism can improve the possibilities of determining the optimal conditions for preparation of biphenyls.

RESULTS

The decarboxylation of copper(I) 2-nitrobenzoate as well as that of copper(I) 4-nitrobenzoate gave good first order kinetics until 85 % reaction as judged from the carbon dioxide evolution. The reaction was studied over a 40° temperature range at four temperatures for copper(I) 2-nitrobenzoate and over a 50° temperature range at four temperatures for copper(I) 4-nitrobenzoate. The apparent first-order rate constants are given in Table 1 and 2. Some representative plots are shown in Fig. 1. The activation parameters at the
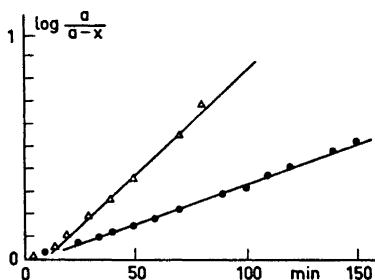

Fig. 1. First-order plots for carbon dioxide evolution. $\triangle$, o-nitrobenzoate at 130°; $\bullet$, p-nitrobenzoate at 200°; a, theoretical stoichiometric weight of carbon dioxide; x, carbon dioxide weight corresponding to different values of time.

mean temperatures, in the Eyring equation, were calculated for the decarboxylation of the two copper salts (Table 3). Using copper(I) salts in the presence of copper powder, it was also possible to observe the catalytic effect of Cu°.

In spite of the good first-order plots obtained it was obvious that the rate constants were strongly dependent upon the initial concentration of the salts (Table 4), the reaction being more rapid for low initial concentrations. This indicates that the solvent participates markedly in the reaction, although as yet no detailed study of the rate constants as functions of the quinoline concentration has been performed.

Table 1. First-order rate constants for the decarboxylation of copper(I) 2-nitrobenzoate in quinoline until 85 % completion. Initial concentration 0.4 M.

Temperature °K	$k \times 10^4$ sec^{-1}
393	1.57 ± 0
403	3.46 ± 0.08
413	7.1 ± 0.2
423	10.9 ± 0.3
433	17.2 ± 0.6

Table 2. First-order rate constants for the decarboxylation of copper(I) 4-nitrobenzoate in quinoline until 85 % completion. Initial concentration 0.4 M.

Temperature °K	$k \times 10^4$ $\mathrm{sec^{-1}}$
453	0.585 ± 0.002
473	$1.38 \ \pm 0.02$
493	$2.86 \ \pm 0.07$
503	$4.61 \ \pm 0$

Table 3. Activation parameters for the decarboxylation of copper(I) nitrobenzoates at mean temperature (T) for each series of experiments.

	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}	$\Delta G^{\ddagger}$ kcal mol^{-1}	T °K
2-Nitrobenzoate	20 ± 1	-26 ± 1	30 ± 1	413
4-Nitrobenzoate	17 ± 1	-40 ± 1	33 ± 1	480

Table 4. "Apparent first-order rate constants" for the decarboxylation of 2-nitrobenzoates.

	Temperature °K	Concentration of 2-nitro-benzoates M	$k \times 10^{-4}$ sec^{-1}	Total time min	Yield CO$_2$ %
Copper(I) 2-nitro-benzoate + copper powder	393	0.4	$2.96 \ \pm 0.05$	270	97
Copper(I) 2-nitro-benzoate + 2-nitro-benzoic acid*	423	0.0057	0.264 ± 0	360	42
Copper(I) 2-nitro-benzoate + 2-nitro-benzoic acid *	423	0.144	$10.3 \ \ \pm 0.5$	60	95
Copper(I) 2-nitro-benzoate	433	0.016	$31.0 \ \ \pm 7$	50	100
Sodium 2-nitro-benzoate	503	0.4	0.675 ± 0.06	240	57

* Initial acid conc. 0.4 M.

The decarboxylation products were determined in all experiments. Nitrobenzene was the main product from both acids. This indicates proton abstraction from the solvent or from other compounds present. The formation of the corresponding symmetrical nitrobiphenyls (and metallic copper) during copper-

promoted decarboxylation of 2-nitrobenzoic acid and 2,4-dinitrobenzoic acid has previously been described.[1,3,5] Decarboxylation of 0.4 M solution of copper(I) 2-nitrobenzoate in quinoline gives about 65 – 70 % yield of nitrobenzene, 20 % of 2,2'-dinitrobiphenyl, and about 5 % of 2-nitrodiphenylamine. During the decarboxylation of a 0.016 M solution of copper(I) 2-nitrobenzoate in quinoline no evidence of the formation of 2,2'-dinitrobiphenyl was obtained. Decarboxylation of copper(I) 4-nitrobenzoate gave mainly nitrobenzene (about 70 %) and no 4,4'-dinitrobiphenyl.

The temperature equilibria in the runs at the beginning of the experiments were established within 7 to 10 min. The temperature of the metal bath was kept constant to $\pm 1°$ during the experiments. Some differences between the temperatures in metal bath and reaction flask were noticed (about $\pm 1°$). The reproducibility of the experiments was checked in two systems at $140°$ for 2-nitrobenzoate and at $220°$ for 4-nitrobenzoate and was found to be of the order of 1 %. As the result of all these errors the general average deviations were estimated at 5 %.

DISCUSSION

The kinetic studies in the present work concern the course of reactions until 85 % completion. Acceleration of the reaction velocity between 85 % and 100 % completion can perhaps be attributed to additional catalysis by metallic copper formed in secondary reactions. The data in Tables 1, 2, and 3 indicate that the copper-catalyzed decarboxylation is first-order in copper(I) nitrobenzoates.

Cohen and Schambach[5] recently proposed first-order kinetics for the decarboxylations of copper(I) and copper(II) carboxylates. No values for reaction constants were, however, given.

The enthalpies of activation can be compared with the heat of activation for the decarboxylation of 2,4,6-trinitrobenzoic acid in various solvents[6] ($E = 25$ to 35 kcal/mol).

The suggested ordered transition state is supported by the high negative values for the entropies of activation. If a cyclic transition-state complex is formed from the non-cyclic reactants, the entropy of activation will be negative. This apparently happens in Cope rearrangements[7] ($\Delta S^{\ddagger} = -11$ to -14 cal deg^{-1} mol^{-1}). The negative activation entropies in decarboxylations of copper(I) nitrobenzoates would thus be in agreement with cyclic transition states as indicated in eqn. 2.

$$(2)$$
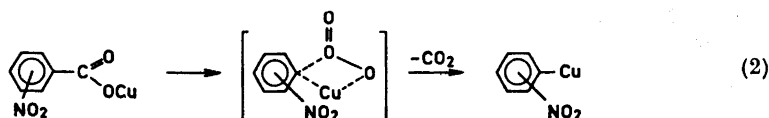
However, the magnitude of the negative values indicates that this explanation is not sufficient. Participation of the solvent and a considerable degree of order of quinoline molecules in the transition state must also be considered.

Organocopper intermediates can be expected to be solvated by quinoline. In addition, other interactions between the quinoline and the acid are possible; these are currently being explored.

During the last years kinetic studies of the reaction of copper(I) acetylides with iodoarenes have also been presented. Activated complexes with a high degree of order in the coupling of iodoarenes with copper(I) acetylides were assumed, and large negative entropies were presented [8] ($\Delta S^{\pm} = -29$ to -63 cal deg^{-1} mol^{-1}). Here, also solvent participation should be considered.

EXPERIMENTAL

Melting points were determined on a micro hot stage. Infrared spectra were recorded on a Perkin Elmer No. 421 instrument and gas chromatograms on an Aerograph 204 − 1B with 5 or 10 % SE Chromosorb W. First-order rate constants and activation parameters were computed on Olivetti Programma 101 P 203 by the method of least squares. The products were also analyzed by thin-layer chromatography on silica gel using mainly toluene as developer. Synthetic quinoline ("min. 99 % puriss.") was purified by extracting a solution in hydrochloric acid several times with ether. The solution was rendered alkaline and the quinoline recovered, dried and distilled.

General procedure. A reaction flask (100 ml) was fitted with a reflux condenser and a nitrogen inlet tube, extending to the bottom of the vessel. The condenser was connected to an absorption train with a U-tube containing activated charcoal and anhydrous magnesium perchlorate. This in turn was connected *via* a three-way valve to tubes for carbon dioxide absorption (Ascarite and magnesium perchlorate). The Ascarite tubes were weighed at intervals. In all experiments quinoline was used as a solvent. The nitrogen flow was kept constant at approx. 8 ml/sec. In all experiments the metal-bath was brought to the desired temperature before the charged reaction flask was immersed. The reaction was carried out at various temperatures; between 120 and 160° for copper(I) 2-nitrobenzoate, and between 180 and 230° for copper(I) 4-nitrobenzoate, until 80 − 90 % of the theoretical evolution of carbon dioxide. The technique used in studying the decarboxylation mixture has been described previously.[3]

At each temperature level the amount of carbon dioxide at various time intervals was computed according to the rate equation of first-order reaction. In every experiment the values thus obtained fit the linear function until 85 % completion.

From the line slopes, specific reaction velocity constants for various temperatures were calculated. The results of the progressing calculations were fitted to the equation for unimolecular gas phase reactions at constant pressure (3).[9]

$$k = \varkappa e(k'T/h)\exp(\Delta S^{\pm}/R)\exp(-\Delta H^{\pm}/RT) \tag{3}$$

In order to calculate the thermodynamic quantities characterizing the activated complex, log (k/T) was plotted *versus* $(1/T)$. The slope of this line is $= -\Delta H^{\pm}/R$ 2.303. If we determine s by fitting the equation $k = s \exp(-\Delta H^{\pm}/RT)$ to the experimental data and set $s = k'T/h \exp(\Delta S^{\pm}/R)$ and solve for $\Delta S^{\pm}$, we obtain $\Delta S^{\pm} = R \ln s - R \ln (k'T/h)$.

These results, assuming that the transition coefficient ($\varkappa$) was unity, are summarized in Table 3. The temperature values used in the equation are equal to the mean temperature for each series of experiments.

Decarboxylation of copper(I) 2-nitrobenzoate at temperatures between 120 and 160°. Copper(I) 2-nitrobenzoate (0.01 mol) was heated in quinoline (25 ml) at various temperatures between 120 and 160°. The reaction times varied from 50 to 270 min. The CO$_2$ yield was about 100 %. The main products were: 67 − 70 % yield of nitrobenzene, 20 % of 2,2'-dinitrobiphenyl and about 5 % of 2-nitrodiphenylamine.

Copper(I) 2-nitrobenzoate and copper at 120°. Copper(I) 2-nitrobenzoate (0.01 mol), copper powder (electrolytic grade, 0.01 mol), and quinoline (25 ml) were kept at 120° for 100 min. The CO$_2$ yield was 100 %.

Copper(I) 2-nitrobenzoate and 2-nitrobenzoic acid at 150°. Copper(I) 2-nitrobenzoate (0.00014 mol) and 2-nitrobenzoic acid (0.01 mol) in quinoline (25 ml) were kept at 150° for 360 min. The CO$_2$ yield was 42 %. Separation on silica gel with 20 % toluene in light

petroleum (b.p. 40 – 60°) gave: nitrobenzene (0.35 g, 70 %); 0.1 g of a yellow-coloured liquid product. The IR spectrum showed a band at 1730 cm^{-1}. The product was not further identified. No evidence of the presence of 2,2'-dinitrobiphenyl was obtained.

Copper(I) 2-nitrobenzoate and 2-nitrobenzoic acid at 150°. Copper(I) 2-nitrobenzoate (0.0037 mol) and 2-nitrobenzoic acid (0.01 mol) in quinoline (25 ml) were kept at 150° for 60 min. The CO_2 yield was 95 %, GLC showed a peak corresponding to nitrobenzene and one peak analogous to that of the unidentified liquid product formed during previous decarboxylation.

Copper(I) 2-nitrobenzoate at 160°. Copper(I) 2-nitrobenzoate (0.002 mol) was heated in quinoline (125 ml) at 160° for 30 min. The CO_2 yield was 95 %. Separation on silica gel with 20 % toluene in light petroleum (b.p. 40 – 60°) gave: nitrobenzene (0.85 g, 69 %) 2-nitrodiphenylamine (0.06 g, 7 %) and some high-molecular products which were not further investigated. No evidence of the presence of 2,2'-dinitrobiphenyl was obtained.

Sodium 2-nitrobenzoate at 230°. Sodium 2-nitrobenzoate was heated in quinoline (25 ml) at 230° for 240 min. The CO_2 yield was 57 %. GLC showed one peak corresponding to nitrobenzene and one peak analogous to that of the unidentified liquid product formed under decarboxylation of copper(I) 2-nitrobenzoate in the presence of 2-nitrobenzoic acid.

Copper(I) 4-nitrobenzoate. 4-Nitrobenzoic acid (0.2 mol) and copper(I) oxide (0.1 mol) were boiled in toluene (ca. 300 ml) for 24 h under nitrogen. The water (1.4 ml) was continuously removed by azeotropic distillation. The yellow product was filtered off and extracted with toluene to remove the traces of unreacted acid and copper(II) bis(4-nitrobenzoate) H_2O. The copper(I) salt was vacuum-dried to constant weight, yield 95 %. The IR spectrum showed that the product was free from acid. The product was analyzed by titration of copper with 0.01 M EDTA solution at pH 7 – 8 and using murexide as indicator, after treatment with nitric acid. The results were in accordance with elemental analysis. (Found: Cu 27.6; N 5.9. Calc. for $C_7H_4NO_4Cu$: Cu 27.7; N 6.1.)

Decarboxylation of copper(I) 4-nitrobenzoate at temperatures between 180 and 230°. Copper(I) 4-nitrobenzoate (0.01 mol) was heated in quinoline (25 ml) at various temperatures between 180 and 230°. The reaction times varied from 360 min to 120 min. The CO_2 yields varied from 73 % to 100 %. GLC and TLC showed mainly nitrobenzene (ca. 0.8 g, 70 %). Separation on silica gel with 20 % toluene in light petroleum (b.p. 40 – 60°) gave about 0.15 g of a crystalline substance, m.p. 98 – 100°, after sublimation. The IR spectrum showed two characteristic ester bands near 1730 cm^{-1}. The last product obtained from the separation was also a crystalline substance (ca. 0.1 g), m.p. 185 – 187°, after sublimation. The IR spectrum showed two characteristic bands at 1650 cm^{-1} and 1730 cm^{-1}. The mass spectrum showed the parent ion at m/e 270. The product was not further investigated.

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