

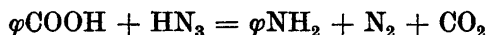
Kinetics of the Reaction between Hydrazoic Acid and Phenanthrenequinone

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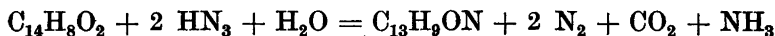
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It is shown that the reaction between hydrazoic acid and phenanthrenequinone consists of two separate reactions. In the first reaction hydrazoic acid and phenanthrenequinone react to give diphenamic acid and nitrogen. In the second reaction diphenamic acid takes part in a normal Schmidt reaction, giving phenanthridone, ammonia, nitrogen, and carbon dioxide.

In a previous communication¹ S. Veibel and the present author have described the stoichiometry of the reaction between phenanthrenequinone and hydrazoic acid as compared with that of the normal Schmidt reaction. The latter is, with benzoic acid as an example:



The former is more complicated, ammonia being formed together with phenanthridone:



In this paper the comparison between the two reactions will be based upon kinetic investigations.

TECHNIQUE

Both reactions have been followed in a Brønsted shaking apparatus of the type described earlier in this journal². Besides that, the second reaction was in a single run followed by titration of the ammonia formed.

The solvent was in all cases concentrated sulfuric acid (81.32–98.53 % H_2SO_4), the concentration of which was determined by titration immediately before the process was started. Owing to the small concentration of quinone and hydrazoic acid the concentration of water can be considered constant during the reaction.

An experiment showed that the spontaneous decomposition of hydrazoic acid is very slow compared to the reactions investigated, thus making any correction for pressure increment due to this reaction unnecessary.

The volume of the shaking apparatus was determined by measuring the increase in pressure, when a weighed amount of sodium azide was oxidized by ceric sulfate in excess in aqueous solution.

In a standard experiment 1.000 millimole sodium azide dissolved in 19.66 ml sulfuric acid reacts with 0.500 millimole quinone. The pressure increase was calculated from the above mentioned data to be 22.19 cm Hg of which 15.54 cm Hg is nitrogen and 6.65 cm Hg is carbon dioxide. The calculation is based upon the following Bunsen absorption-coefficients³ for nitrogen and carbon dioxide in 95.6 % sulfuric acid: $\alpha_{N_2} = 15.55 \cdot 10^{-3}$; $\alpha_{CO_2} = 0.923$.

KINETICS

The reaction between benzoic acid and hydrazoic acid

Table 1 shows that the second order scheme is followed exactly to a degree of advancement of 0.65 with a velocity constant of $0.198 \cdot 10^{-3} \text{ l mole}^{-1} \text{ sec}^{-1}$.

Table 1. The reaction between benzoic acid and acid and hydrazoic acid. 1 millimole of benzoic acid and 1 millimole of hydrazoic acid in 19.66 ml sulfuric acid (95.4 % H_2SO_4). 25.00° C.

<i>t</i> min	ξ	$\frac{19.66}{60} (1-\xi^{-1})-1$	$k \cdot 10^3$ l mole ⁻¹ sec ⁻¹
50	0.029	0.010	0.20
100	0.057	0.020	0.20
150	0.083	0.030	0.20
200	0.109	0.040	0.20
300	0.157	0.061	0.203
400	0.194	0.079	0.198
500	0.233	0.100	0.200
1 400	0.441	0.259	0.185
1 700	0.505	0.334	0.196
2 000	0.548	0.397	0.199
3 000	0.649	0.606	0.202

mean value: $0.198 \cdot 10^{-3} \text{ l mole}^{-1} \text{ sec}^{-1}$

The only available data for the influence of substituents on the velocity are those of Briggs and Lyttleton⁴. These are not very accurate and refer to a heterogenous reaction, they are therefore difficult to interpret, and it was a tempting task to determine the velocity constant for some substituted benzoic acids. It proved very difficult to obtain reproduceable results, presumably because the substituted acids decomposed in the sulfuric acid solution (dark colour). The only reliable result is the constant for *p*-methyl-benzoic acid which was found to be $0.371 \cdot 10^{-3} \text{ l mole}^{-1} \text{ sec}^{-1}$ in 95.4 % sulfuric acid at 25.00° C.

This indicates that if the Hammett equation⁵

$$\log k_{\text{subst}} - \log k_{\text{unsubst}} = \sigma \cdot \rho$$

is valid, we must think of ρ as having a comparatively great negative value.

The reaction between phenanthrenequinone and hydrazoic acid shows a sharp decrease in velocity at a degree of advancement of about one third, cf. Fig. 1. This indicates that the reaction cannot be described by a mechanism involving only intermediate products in quasi-stationary concentrations.

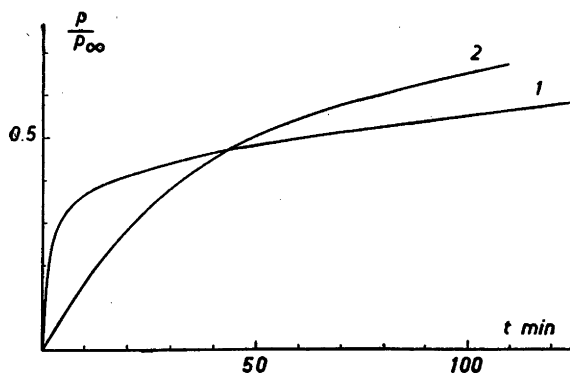
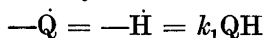


Fig. 1. Gas evolution as function of time for the reaction between hydrazoic acid and 1. phenanthrenequinone, 2. retenequinone.

Systematic guessing on chromometric integrals⁶ is thus out of place, as it can be considered impossible to guess the very complicated functions which arise from mechanisms with intermediates in non-stationary concentrations.

A better way out would probably be to investigate the reaction at the very beginning and at the end. Whereas the former always will give some indication, the latter will only give interpretable results if the last measurable velocity constant is small compared to all the others.

Fig. 2 shows in arbitrary units the initial velocity as function of the concentrations of quinone and hydrazoic acid. It is evident that the first measured step in the reaction is described by:



where Q and H denote concentrations of quinone and hydrazoic acid respectively.

The following equation between pressure and time which is valid at the end of the reaction shows that the last part of the process also can be described by a second order expression.

$$\left(1 - \frac{p(t) - \pi}{p_{\infty} - \pi}\right)^{-1} - 1 = k_2(t - \tau)$$

π and τ are constants which have the dimension of pressure and time respectively.

To investigate the nature of the four constants (k_1 , k_2 , π , τ) experiments with different water contents in the sulfuric acid were carried out. Whereas π proved to be almost constant ($\sim \frac{1}{3} \cdot p_{\infty}$), it was found that k_1 and k_2 and τ vary greatly, but in such a manner that $k_1 \cdot \tau$ is roughly constant.

As analysis showed the gas evolved in the beginning of the reaction to be almost pure nitrogen, π was taken to be 7.77 cm Hg which is equivalent to half of the nitrogen that should be evolved according to the stoichiometry. Doing so we are forced to interpret τ , the "starting time" of the last reaction, as the

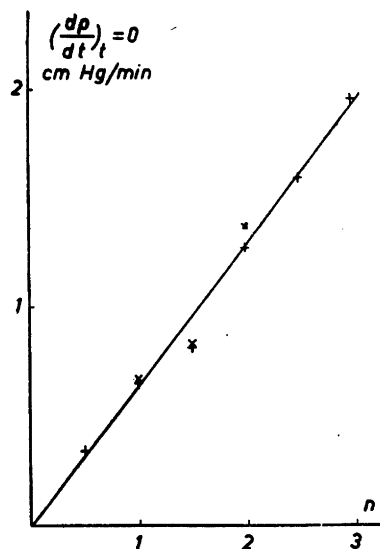
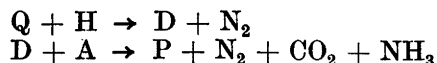


Fig. 2. Initial velocity of the reaction between hydrazoic acid and phenanthrenequinone as function of the initial concentrations.



time required to generate a compound that reacts according to this scheme. As mentioned above, $k_1\tau$ is roughly independent of the sulfuric acid concentration, indicating that all reactions occurring between the measured initial reaction and the measured last reaction are rapid as compared to these two. Table 2 shows the velocity constants as functions of the sulfuric acid concentration.

The reaction was in a single run followed by titration of the ammonia formed. It proved that the ammonia is released by a second order reaction with equivalent amounts of the reactants, and that the velocity constant equals k_2 . We have thus established this scheme of reactions:



where P is phenanthridone and D is some intermediate in nonstationary concentration.

Table 2. The velocity constants as functions of the sulfuric acid concentrations. 25.00° C.

Experiment No.	% H ₂ SO ₄	k_1 l·mole ⁻¹ ·sec ⁻¹	$k_2 \cdot 10^3$ l·mole ⁻¹ ·sec ⁻¹	τ sec
12	98.53	0.041	3.58	1 900
14	96.81	0.113	2.17	250
15	96.81	0.115	1.99	750
17	95.41	0.157	1.60	600
21	92.53	0.382	1.02	200
20	84.32	2.32	0.76	50

Mathematical treatment

If we by x denote the number of moles of hydrazoic acid which react according to the first reaction, and by y denote the number of moles of hydrazoic acid which reacts according to the second reaction, then we have for the reaction between equivalent amounts

$$\begin{aligned}\dot{x} &= k_1(2-x-y)(1-x) \\ \dot{y} &= k_2(2-x-y)(x-y)\end{aligned}$$

Dividing and substituting k_1/k_2 by k we get

$$\frac{dy}{dx} = k \frac{x-y}{1-x} \quad \text{or} \quad y = \frac{1-kx}{1-k} - \frac{1}{1-k} (1-k)^k$$

and from this and the first equation we get:

$$k_1 t = \int_0^x \frac{dz}{\frac{1}{1-k} (1-z)^{1+k} + \frac{1-2k}{1-k} (1-z)^2}$$

As we have $p(t)/p_\infty = \xi(t) = 0.350 x + 0.650 y$, a numerical evaluation of this integral can give us the theoretical values of $p = p(t)$.

Owing to the fact that $k \ll 1$ this evaluation is very tedious and is omitted in favour of the following proof.

Let the reaction be carried out between 2 moles of hydrazoic acid and n moles of phenanthrenequinone. We then have

$$\begin{aligned}\dot{x} &= k_1(2-x-y)(n-x) \\ \dot{y} &= k_2(2-x-y)(x-y)\end{aligned}$$

$$\text{from which } y = \frac{n-kx}{1-k} - \frac{n^{1-k}}{1-k} (n-x)^k$$

This equation is also valid for the values (x_∞, y_∞) reached when $t \rightarrow \infty$. For these values we further have: $x_\infty = y_\infty = 2$, as a total amount of 2 moles of hydrazoic acid is converted. For the apparent final degree of advancement $\xi^* = p_\infty/22.19$ defined as the ratio of the final pressure to the final pressure in a reaction between equivalent amounts of quinone and hydrazoic acid, we still have $\xi^* = 0.350 x_\infty + 0.650 y_\infty$.

Table 3. Final pressure as function of the initial concentration of quinone. Solvent: 98.53 % sulfuric acid. 25.00° C.

n = moles of quinone pro 2 moles of hydrazoic acid	p_∞	ξ^* exptl.	ξ^* theor.
1.0	22.17	0.999	1.000
1.5	18.64	0.840	0.835
2.0	16.90	0.762	0.765
2.5	16.43	0.740	0.739
3.0	16.17	0.729	0.729

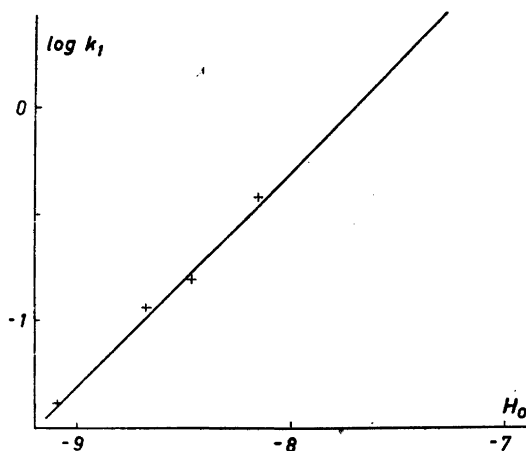


Fig. 3. $\log k_1$ plotted against Hammett's H_0 acidity function.

By substitution we arrive at the following equation between ξ^* and n in which has been used the value $k = 0.087$ corresponding to the experiment.

$$n + 1.753 - 2.753\xi^* - n^{0.913}(n - 4.333 + 3.333\xi^*)^{0.087} = 0$$

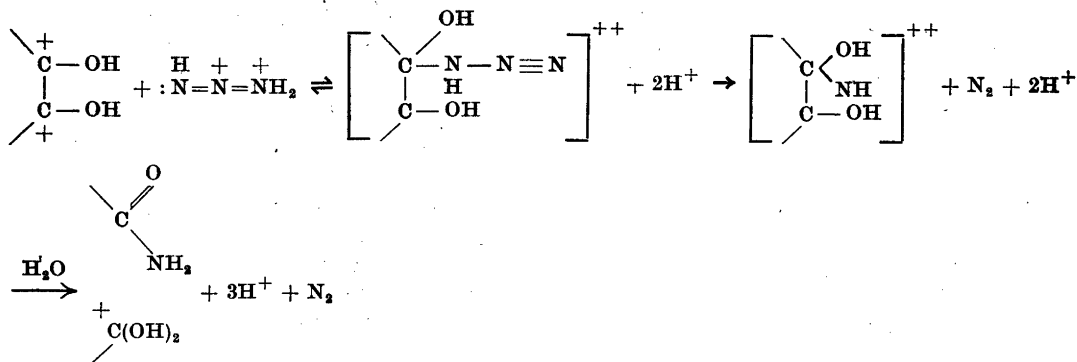
The experimental values are given in Table 3 together with the theoretical values determined by iteration. The agreement is quite satisfactory and gives good evidence for the correctness of the postulate.

Mechanism

1. Fig. 1 shows the velocity of the first reaction to be proportional to the product of the concentrations of quinone and hydrazoic acid. The velocity constant k_1 decreases very markedly, when the concentration of sulfuric acid is increased. To get an estimate of this variation we can plot $\log k_1$ against Hammett's H_0 acidity function⁷. This is in principle incorrect, as H_0 measures the tendency of a solution to transfer a proton to a neutral base, and we know that most of the quinone and the hydrazoic acid will be found as highly protonized ions, such as: $C_{14}H_8O_2H_2^{++}$ and $H_4N_3^{++}$. As the plot gives a straight line we assume however that in this dilute solution of water in sulfuric acid certain regularities, such as $H_0 \sim H_+ \sim H_{++}$ will be found.

In this case the slope of the line should be an integer and Fig. 2 shows it to be +1, which means that the reaction velocity is inversely proportional to the "hydrogen ion concentration". The most reasonable explanation of this fact is that the reaction involves the ion $H_3N_3^{++}$ which is the most highly protonized form of hydrazoic acid that still possesses a lone pair.

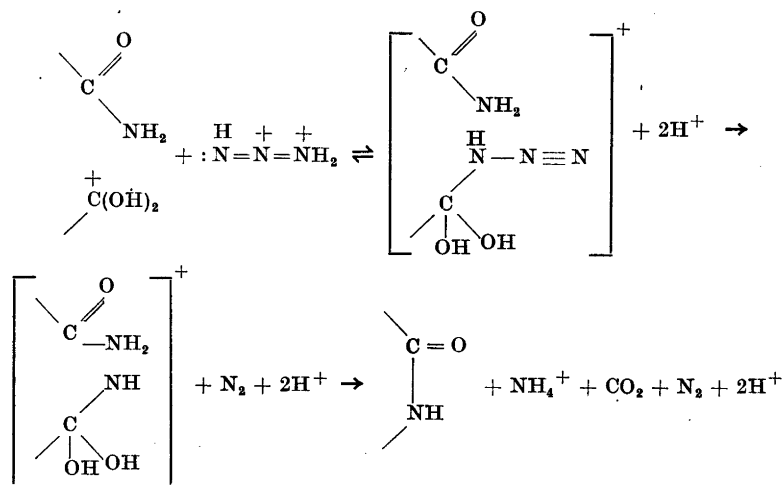
In order to prove that the last molecule in this sequence is the above-mentioned intermediate, the reaction mixture was diluted with ice and water. A white precipitate was formed, which showed no depression in melting point



when mixed with an authentic sample of diphenamic acid, prepared according to standard methods⁸. As the yield was practically quantitative, we have thus confirmed the proposed mechanism, in which we consider the second step as rate determining.

2. As the intermediate is a substituted benzoic acid, the relation to the normal Schmidt reaction has now been established.

A rough estimate of the heat of activation based upon experiments at 25.00° C and 30.00° C showed it to be 27 000 cal. for the last reaction, which is in good agreement with the heat of activation for similar reactions, such as Curtius and Lossen rearrangements⁹. The above mentioned value of ρ is also in reasonably good agreement with values of ρ found for these reactions¹⁰. The following mechanism is therefore proposed:



3. The interesting case of 1-methyl-7-isopropyl-phenanthrenequinone (retenequinone) demands further discussion. It reacts with hydrazoic acid to give only one compound, and not two isomer compounds as could be expected. In terms of the proposed mechanism this is explained as follows:

In the first reaction that CO group which is near to the methyl group has a very low reactivity due to steric hindrance. The intermediate product will thus be predominantly 3-methyl-4'-isopropyl-22'-diphenic acid(2')monamide. In this compound the carboxy group is sterically screened by a phenyl group and a methyl group, and thus ionizes to $-\overset{+}{C} = O$ instead of $-\overset{+}{C}(\text{OH})_2$ in sulfuric acid ¹¹.

It is however known that the former of these ions reacts more rapidly with hydrazoic acid, than does the latter ¹². It is thus seen that it is also a consequence of the mechanism that the reaction with retenequinone should be slower at the beginning of the reaction and more rapid towards the end, than is the corresponding reaction with unsubstituted phenanthrenequinone. The experiments confirm this result (Fig. 1).

The fact that k_1 and k_2 are approaching each other, render it very difficult to split up the experimental results into two reactions. But still we can find k_2/k_1 from the relation between ξ^* and n if we, in an experiment with excess of quinone, know the final pressure. From a single experiment in 95.4 % sulfuric acid was found $k = 0.98$, which confirms the previous considerations.

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Note added in proof. Professor Veibel has informed the author that a paper related to the same research has just been published by other authors (Badger, G. M. and Seidler, J. H. *J. Chem. Soc.* 1954 2329). These authors have studied the reaction between hydrazoic acid and crysenequinone from the point of view of its use in the preparation of phenanthridone, and have isolated the amidoacid as an intermediate product.

In the reaction only one phenanthridone is formed, and the reaction is thus analogous to that between hydrazoic acid and retenequinone. It therefore seems very probable that the two rate constants will behave in the same manner as the rate constants of the latter reaction, k_1 being smaller and k_2 greater than the corresponding rate constants of the reaction between hydrazoic acid and phenanthrenequinone.

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