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Homogeneously Catalyzed Hydrogenation of Quinones and Aromatic Radical Cations with Alkanes

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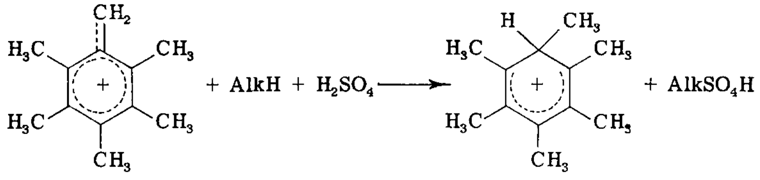
Pentamethylbenzyl cation, dissolved in a strong proton acid, is a powerful catalyst for hydrogenation of quinones and aromatic radical ions by alkanes. The catalytic process consists of two steps, which can be studied separately. In concentrated sulfuric acid, the pentamethylbenzyl cation, for instance, reacts with alkanes yielding protonated hexamethylbenzene. In its turn protonated hexamethylbenzene transfers hydrogen to quinones or to aromatic cations with regeneration of the pentamethylbenzyl ion.

INTRODUCTION

Hydrocarbons of the methane series are known as inert substances. It requires a powerful catalyst like $AlCl_3 \cdot HCl$ to provoke isomerization reactions at room temperature or at lower temperatures. For other reactions such as dehydrogenation with quinones higher temperatures are needed. As an example we mention that a quinone with a high oxidation-reduction potential like chloranil can be used to produce olefins, but not below 130°C (*1*).



(A$^+$)

(AH$_2^+$)

However, the recently discovered pentamethylbenzyl cation (A^+) dissolved in a strong acid, concentrated H_2SO_4 for instance, is a powerful hydrogen acceptor for alkanes even at room temperature or at lower temperatures (*2*). With the exception of methane the alkanes react readily. In the case of methane the rate of conversion is low.

The reactions proceed via the transfer of a hydride ion form the alkane (AlkH) to the A^+ ion accompanied by the addition of a proton from the acid. This results in the formation of protonated hexamethylbenzene (AH_2^+).

In its turn AH_2^+ is able to transfer hydrogen to a quinone (Q), regenerating A^+. The sequence of these two steps constitutes catalytic hydrogen abstraction from the alkane by a quinone which takes place even at low temperatures.

The pK_a value of protonated hexamethylbenzene (*3*) is -9.10. This implies that in concentrated H_2SO_4 ($H_0 = -10.0$) the protonation of hexamethylbenzene is nearly complete.* This protonation contributes

First step:
$$A^+ + AlkH + H_2SO_4 \longrightarrow AH_2^+ + AlkSO_4H \tag{1}$$

Second step:
$$AH_2^+ + Q \longrightarrow A^+ + QH_2 \tag{2}$$

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* The pK_a is defined by $pK_a = H_0 + \log [AH_2^+]/[AH]$, where H_0 is the Hammett acidity function.

essentially to the driving force of the reaction (1). Comparison with similar reactions of related benzyl cations shows that a high pK_a value of the proton complex formed favors an increase of the rate of hydrogen transfer (*2*, *4*).

The second step is not restricted to quinones. Positive aromatic radical ions (Ar^+) may also take up hydrogen, thereby forming proton complexes (ArH^+) of the parent aromatic hydrocarbons. Reaction (2) is then replaced by reaction (3)

$$AH_2^+ + 2\,Ar^+ \longrightarrow A^+ + 2\,ArH^+ \qquad (3)$$

In this case it is the degree of basicity of the aromatic hydrocarbon (Ar), which determines whether the reaction takes place at a measurable rate.

Catalytic hydrogen transfer will be described for three acceptor systems: (1) heated sulfuric acid; (2) positive aromatic radical ions; (3) quinones.

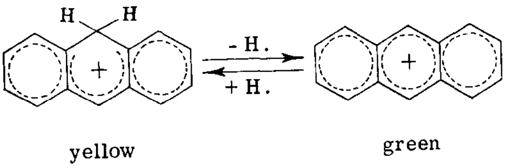
RESULTS

Reactions of heated sulfuric acid. On warming a solution of hexamethylbenzene in H_2SO_4 the yellow color of the protonated hexamethylbenzene changes into purple, due to the formation of the pentamethylbenzyl cation:

$$AH_2^+ + 3\,H_2SO_4 \longrightarrow A^+ + 2\,H_3O^+ + 2\,HSO_4^- + SO_2 \qquad (4)$$

After cooling of the solution addition of an alkane results in a rapid reaction. The color changes from purple into yellow. The warm solution reacts only slowly because the high temperature opposes the protonation of hexamethylbenzene which would be formed by a hydride ion transfer from the alkane to the pentamethylbenzyl ion.

Reactions of positive aromatic radical ions. Proton complexes of aromatic hydrocarbons can be oxidized to positive radical ions (*5*).



(5)

The converse reaction, the uptake of a hydrogen atom, will be correlated with the electron affinity of the radical ion and the basicity of the aromatic molecule. The latter quantity proves to be the more important one, as will be discussed further on. Therefore the positive radical ion of tetracene, a very basic hydrocarbon, is one of the strongest hydrogen acceptors among the aromatic hydrocarbon radical ions.* Nevertheless this radical ion dissolved in H_2SO_4 does not react with alkanes. However, addition of the pentamethylbenzyl cation to this system leads to a catalyzed reaction in which fairly rapid hydrogen transfer from the alkane to the tetracene action with formation of protonated tetracene occurs. Now reaction (1) is accompanied by

Reaction of quinones. When diphenoquinone is dissolved in H_2SO_4, the divalent positive ion of 4,4′-dihydroxydiphenyl is formed (*6*). This ion can be reduced to 4,4′-dihydroxydiphenyl by strong hydrogen donors such as protonated hydrocarbons, which are converted into the corresponding positive radical ions (*7*).

Protonated hexamethylbenzene reacts differently in so far as it loses two electrons and two protons, yielding the pentamethylbenzyl cation.

Reaction (7) combined with reaction (1) again gives a catalytic hydrogen transfer process, this time from alkane to diphenoquinone.

4,4′-Dihydroxydiphenyl formed according to (7) might react further with the pentamethylbenzyl cation yielding an arylation product, thus removing the catalyst. At room temperature, however, 4,4′-dihydroxydiphenyl is sulfonated very rapidly thereby becoming unreactive towards the catalyst.

Other quinones react similarly. The quinones investigated were *p*-quinone, α-naphthoquinone, and anthraquinone. It appeared that the rate of hydrogen transfer depends on the normal oxidation-reduction potential. As the value of the normal oxidation-reduction potential increases hydrogen transfer becomes faster:

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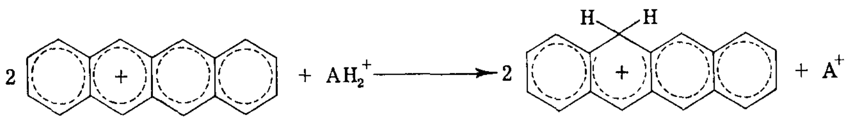
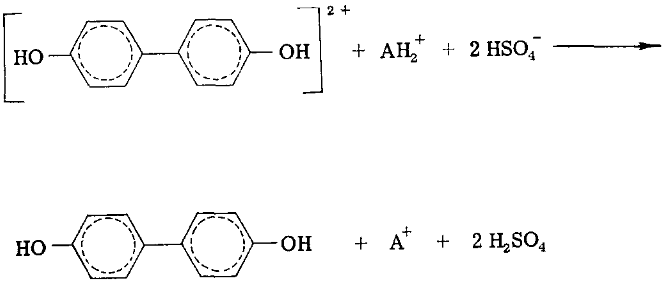
* Tetracene dissolves in H_2SO_4 with formation of a proton complex. After some time the proton complex is converted into the positive radical ion.



(6)



(7)

$$k_{\text{diphenoquinone}} > k_{p\text{-quinone}} > k_{\alpha\text{-naphthoquinone}} > k_{\text{anthraquinone}} \quad (8)$$

Discussion

As mentioned previously (see "Reactions of positive aromatic radical ions") the differences between the reactivities of the aromatic radical ions are primarily correlated with the basicities of the corresponding aromatic molecules and to a lesser extent with the electron affinity of the radical ions. This will be discussed by considering the equilibrium between proton complex (ArH^+) and radical ion (Ar^+):

$$ArH^+ \rightleftarrows Ar^+ + H^+ + e \quad (9)$$

According to Aalbersberg *et al.* (*5*) the equilibrium constant (K) can be written as

$$\ln K = \ln \frac{[Ar^+]}{[Ar]} + \ln \frac{[Ar]}{[ArH^+]} + C \quad (10)$$
$$= -\frac{F}{RT}\epsilon_0 - \ln K_b + C$$

or

$$\log K = -16.95\,\epsilon_0 - \log K_b + C' \quad (11)$$

The basicity constants K_b have been determined experimentally by Mackor *et al.* (*8*). The potentials ϵ_0 can be calculated from the polarographic half-wave potentials $\epsilon_{1/2}(Ar^+)$ of the hydrocarbon positive ions in $CF_3COOH–BF_3{\cdot}H_2O$ (29% m) determined by Aalbersberg *et al.* (*9*) according to

$$\epsilon_0 = \epsilon_{1/2}(Ar^+) + C'' \quad (12)$$

Equations (11) and (12) together yield

$$\log K = -\log K_b - 16.95\,\epsilon_{1/2}(Ar^+) + C''' \quad (13)$$

The results of the calculation are collected in Table 1.

TABLE 1

Hydrocarbon	log K_b[a]	16.95 $\epsilon_{1/2}$ (Ar^+)[b]	C + log K
3, 4-Benzopyrene	6.5	−4.41	−2.1
Tetracene	5.8	−5.76	0.0
Anthracene	3.8	−3.90	+0.1
Perylene	4.4	−5.25	+0.9
Pyrene	2.1	(−3.73)	+1.6

[a] Taken from ref. (*8*).

[b] Taken from ref. (*9*); the figure between parentheses is extrapolated.

Comparing column 2 and column 3 it is seen that the variations in log K_b are the more important ones, as was mentioned before.

The hydrocarbons are listed in sequence of increasing log K, which is the same sequence as found for the velocity of reaction (5) from left to right, as has been reported in a previous paper (*7*). Since in the present investigation the velocity of the reverse reaction (5) has been shown to depend on the hydrocarbon in the same way as the velocity of the forward reaction, there is no doubt that the sequence of the equilibrium constants given in Table 1 is correct.

However, Aalbersberg *et al.* (*5*) have calculated the same equilibrium constants but instead of using their own half-wave potentials their calculations were based on oxidation potentials determined by Lund with solutions of hydrocarbons in acetonitrile (*10*). The two sets of potentials are compared in Table 2.

TABLE 2

Hydrocarbon	$\epsilon_{ox}(\mathrm{Ar})$[a]	$\epsilon_{1/2}(\mathrm{Ar}^+)$[b]
Tetracene	0.54	−0.34
Perylene	0.63	−0.31
3, 4-Benzopyrene	0.76	−0.26
Anthracene	0.84	−0.23
Pyrene	0.86	(−0.22)

[a] Taken from ref. (*10*).

[b] Taken from ref. (*9*); the figure between parentheses is extrapolated.

Apparently both columns show the same trend but the differences obey the relation

$$\Delta\epsilon_{1/2}(\mathrm{Ar}^+) \approx 1/3\Delta\epsilon_{ox}(\mathrm{Ar}) \qquad (14)$$

This observation explains the conclusion made in a previous paper, stating that only one-third of Lund's oxidation potentials showed up in the velocity constant of the forward reaction (5) (*7*).

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