50. Rh-Catalyzed Oxidation of Anthracenes with *tert*-Butyl Hydroperoxide. Kinetic Aspects

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The polar effects of substituents on reactivity in oxidation of 2-substituted anthracenes with *tert*-butyl hydroperoxide (TBHP)/$Rh(PPh_3)_3Cl$ have been investigated and compared with those obtained with TBHP/$VO(acac)_2$ and chromic acid. The anthracene reactivities obtained from competition experiments are correlated with *Hammett*'s σ_p-constants. The ρ-values are -2.60 for chromic acid and 0.72 for TBHP/$VO(acac)_2$. A poor correlation with $\rho = -0.17$ ($r = 0.756$) was obtained for TBHP/$Rh(PPh_3)_3Cl$. It is concluded that the Rh-catalyzed reaction does not consist in electrophilic oxygen transfer to the anthracene.

Recently, we discovered that the combination of *tert*-butyl hydroperoxide (TBHP) with $Rh(PPh_3)_3Cl$ converts anthracenes to anthraquinones in high yields [1]. We considered the reaction of some general interest, since the large majority of the recently developed catalytic systems involve transformations of easily oxidizable functional groups such as alcohols, double bonds, while progress in reactions involving aromatic compounds is slow [2]. Although oxidation of anthracene may be of limited practical value, the compound has some favorable features for mechanistic investigations. It is quite reactive and the attack occurs almost exclusively at C(9) and C(10). In addition, the lateral benzene rings prevent further degradation of the final product, anthraquinone, so that only a limited amount of side-products are to be expected. We hoped that mechanistic studies of this model system would provide some insight allowing a more rational approach towards oxidation of other aromatic substrates.

After the discovery of the system $Rh(PPh_3)_3Cl$, some screening experiments were carried out with other systems *(Table)*. The *Wilkinson* catalyst ($Rh(PPh_3)_3Cl$) was the most efficient among the compounds studied for reaction with anthracene. $RuCl_2(PPh_3)_3$ was less suitable, but this complex in conjunction with TBHP oxidizes alcohols and catechols [3]. A kinetic study of anthracene with $Mo(CO)_6$/TBHP has been published, but no yields are indicated [4]. The reaction is accompanied by extensive decomposition of starting material, and we could not increase the yields over 40%. Among the solvents tested, benzene gave best results, followed by chlorobenzene, but no appreciable transformation took place in tetrachloroethylene.

In the Mo- or V-catalyzed epoxidation of alkenes the oxygen transfer takes place from coordinated TBHP to free alkene [5] or, alternatively, *via* peroxymetalation involving coordinated TBHP and π-coordinated alkene [6]. The ρ-value of -1.4 for epoxidation of styrene with Mo(VI)/TBHP is characteristic for an electrophilic oxygen transfer [7]. By analogy we proposed an electrophilic attack at C(9) and C(10) of anthracene for the system $Rh(PPh_3)_3Cl$ [1] *(Scheme)*. This hypothesis is however questionable. For electro-

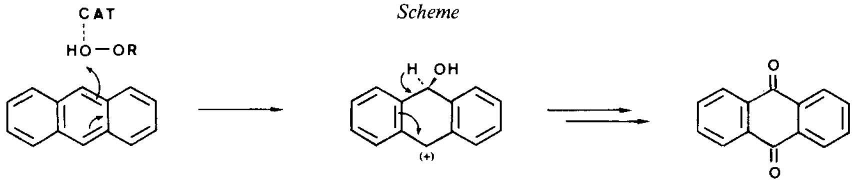
Table. *Efficiency of Catalysts for Oxidation of Anthracene with TBHP*[a])

Catalyst	TBHP [mol-equiv.]	Antraquinone [%]	Recovered anthracene [%]
2.5% $Mo(CO)_6$	3	37	17
2.5% $VO(acac)_2$	3	37	45
1% $IrCl(CO)(PPh_3)_2$	3	15	60
1% $RhCl(CO)(PPh_3)_2$	3	< 40	b)
1% $RuCl_2I(PPh_3)_3$	4	41	b)
1% $RhCl(PPh_3)_3$	4	91	0

[a]) Conditions: 2.8 mmol of anthracene in 100 ml of benzene, $T = 70°$, 48 h. Yields determined by column chromatography.

[b]) Not determined.

Scheme



philic oxygen transfer, the metal of the coordinating complex must be in a high oxidation state [2]. This condition does certainly not apply to the initial stage of the Rh(I)-catalyzed reaction, but it might be fulfilled through oxidation of the complex before oxygen transfer to the organic substrate. Clearly, other mechanisms, in particular of radical nature for which there is ample precedent [8], should be envisioned. We have now investigated the dependency of the reaction from polar substituent effects to get information on the nature of the oxygen transfer.

For substituted benzenes, this approach is well-documented, and a variety of scales reflecting electronic effects of substituents are available [9]. Few exist for anthracenes except for studies concerning influence of substituents at C(9) on those at C(10). The *Dewar-Grisdale* approach could, in principle, be extended to anthracenes, but the significance of the calculated substituent constants is difficult to evaluate because of lack of experimental results. To avoid such difficulties, we have extended our study to include two additional and better understood systems for comparison with TBHP/$Rh(PPh_3)_3Cl$, namely chromic acid and TBHP/$VO(acac)_2$. Relative rates of oxidation of substituted anthracenes were obtained from competition experiments. We have shown in [1] that, for the reactions under investigation, the main product is the quinone; the reactivities determined from the relative amount of unreacted anthracenes, therefore, are related to their oxidation to quinones (see *Exper. Part*). In the case of chromic acid, some rate constants were determined by kinetics under pseudo-first-order conditions with excess substrate. The amount of unreacted Cr(VI) was determined spectrophotometrically *via* the 1,5-diphenylcarbonohydrazide complex [11]. Reproducible first-order plots were obtained for anthracene and its 2-substituted derivatives with electron-donating substituents [12]. Plots for compounds with electron-withdrawing groups deviated from linearity and had to be extrapolated to $t = 0$. The kinetic results agree with those obtained from competition experiments, however, the extrapolated rate constants show too much scatter to be of much use. Tables containing all data are given in [12], and are available from the authors upon request.

Since attack at C(9) or C(10) leads to one and the same product (anthraquinone), the choice of constants becomes ambiguous. For chromic acid the best correlation was obtained with the equation:

$$\log k/k_o = \rho(\sigma_p + \sigma_m)$$

with $\rho = -1.19$ ($r = 0.976$). This equation allows to include 1-substituted and the 2,3-disubstituted anthracenes. However, it requires concerted attack at both C(9) and C(10) [13] for which there is no precedent. On the other hand, the *Hammett* plots for 2-substituted anthracenes using σ_p ($\rho = -2.60$, $r = 0.973$) and σ_p^+ ($\rho = -1.79$, $r = 0.96$) are about as satisfactory. For reasons of simplicity and of absence of detailed mechanistic knowledge concerning the TBHP oxidations, we restrict the discussion to the *Hammett* plot with the σ_p constants *(Figure)*. The slope of the correlation with chromic acid ($\rho = -2.60$) is consistent with an electrophilic attack on the anthracene [14] as shown in the *Scheme*.

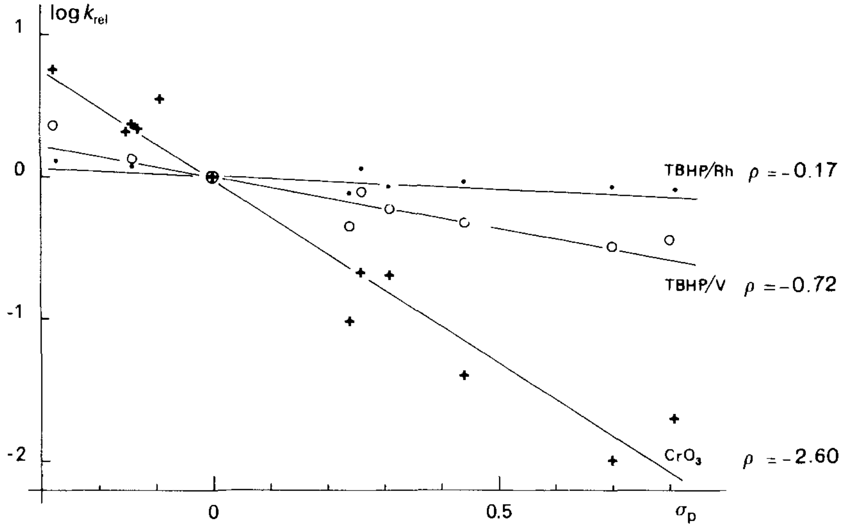


Figure. Hammett *plot for oxidation of 2-substituted anthracenes with chromic acid, TBHP/VO(acac)$_2$ and TBHP/Rh(PPh$_3$)$_3$Cl.* Data from [12].

In comparison, oxidation of substituted styrenes with chromyl chloride is characterized by a reaction constant of $\rho^+ = -2.0$ [15]. On the other hand, anthracene oxidation with TBHP/VO(acac)$_2$ has a significantly smaller, but still negative reaction constant of $\rho = -0.72$. A similar trend, although less pronounced, is observed upon comparison of styrene oxidation with chromyl chloride and epoxidation with TBHP/Mo(VI) ($\rho = -1.4$) [7]. In sharp contrast, anthracene oxidation with TBHP/Rh(PPh$_3$)$_3$Cl shows no significant dependency from electronic substituent effects ($\rho = -0.17$, $r = 0.756$). This result is clearly incompatible with a reaction mechanism involving electrophilic attack *(Scheme)*.

At the present state of knowledge, we cannot advance another mechanism. However, some observations may be of interest: Rh(PPh$_3$)$_3$Cl catalyzes decomposition of hydroperoxides to O_2 and alcohol [16]. This reaction is temporarily inhibited by phenols or pyridine [16] or *N*-phenyl-2-naphthylamine [17]. The mechanism of inhibition could consist either in occupation by the inhibitor of a vacant coordination site of the catalyst, necessary for peroxide decomposition or, alternatively, by scavenging intermediate alkylperoxy radicals and thus breaking the autocatalytic cycle for hydroperoxide decomposition. Similarly, anthracene and its derivatives inhibit decomposition in the system $Rh(PPh_3)_3Cl$ [1] and practically all of the TBHP is consumed for antraquinone formation. In contrast, naphthalene derivatives are inefficient for TBHP decomposition and, in addition, are not oxidized under the reaction conditions. 1,4-Dihydroxynaphthalene and hydroquinone are, however, converted in 60 and 46% yields [1], respectively, to the corresponding quinones. The different comportment of anthracene and naphthalene may be due to their different complexing ability with the metal, or different efficiency for scavenging alkylperoxy radicals. However, neither explanation is satisfactory: the ratio of the equilibrium constant for complexation of anthracene or naphthalene on a (cationic) Rh complex is only *ca.* 6 [18]; if this situation prevails in $Rh(PPh_3)_3Cl$ it does not explain the large difference in yield between the substrates. On the other hand, the absence of correlation with σ-constants is difficult to reconcile with the proposed alkylperoxy radical [16], since the latter exhibits electrophilic properties [19]. Current research is directed towards understanding the significance of substrate binding for the oxidation mechanism.

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Experimental Part

2-Substituted Anthracenes. The following anthracene derivatives were synthesized by literature procedures: 2–OH [20], 2–OCH_3 [21], 2–OAc [21] [22], 2–Cl [23] [24], 2–CN [23] [25], 2–NO_2 [26], 2–Br [23] [24] [27], 2–$COOCH_3$ [28] [29], 1–OMe [21], 1–OAc [22]. All compounds were purified by recrystallization or chromatography and characterized by their physical and spectroscopic data [12] [30].

Anthraquinones from Oxidation of Anthracenes. – General Procedure [1]. – *Chromic Acid.* To a soln. of 0.8 mmol of anthracene in 90 ml 95% AcOH at 30–40° was added dropwise in 15 min 1.6 mmol of $(NH_4)_2Cr_2O_7$ in 1 ml H_2O, 10 ml 95% AcOH and 0.5 ml conc. H_2SO_4. After 15 min, the mixture was poured into 100 ml of H_2O. The precipitate was collected, washed with sat. $NaHCO_3$ and H_2O. The mother liquor was worked up by extraction with $CHCl_3$. The crude anthraquinones were purified by column chromatography. The reported yields [1] refer to isolated material after purification.

TBHP/VO(acac)₂ and TBHP/Rh(PPh₃)₃Cl. To a soln. of 0.56 mmol of anthracene and the respective catalyst (3% $VO(acac)_2$, 4.9 mg; 1% $Rh(PPh_3)_3Cl$, 5.4 mg) in 9 ml of benzene was added at 70°, 1.0–1.1 ml of 2.18M TBHP in benzene dropwise. The soln. was stirred at 70° during 16–48 h. After evaporation of the solvent, the anthraquinones were purified by column chromatography.

Relative Reactivities of Anthracenes by Competition Experiments. – Chromic Acid. Pairs of substituted anthracenes (9.5×10^{-2} mmol each) were dissolved in 100 ml of 95% AcOH, 8×10^{-4}N in H_2SO_4 by ultrasonic vibrations. To 25 ml of this stock soln. was added 1–1.5 ml of 0.0125M Cr(VI) in the same solvent. The mixture was heated to 40° during 30 min. Then, 3 ml of 0.02M CH_3COONa was added. The soln. was evaporated to dryness, and a known amount of standard (high-boiling alkane) followed by *ca.* 5 ml of $CHCl_3$ were added. Dissolution of the org. material was accelerated by ultrasound. After transfer of the liquid into a 10-ml flask, it was concentrated to *ca.* 0.6 ml and analyzed by GC. The response factors of the instrument were determined for each couple of anthracenes according to the standard procedure without adding the chromic acid. All data correspond to average values obtained from 7 injections. The relative reactivity of anthracene B over anthracene A was calculated from the initial and final concentrations using the equation [31]:

$$k_B/k_A = \frac{\ln([B]_t/[B]_o)}{\ln([A]_t/[A]_o)}$$

The reactivities used for the *Figure* are average values calculated relative to unsubstituted anthracene [12].

TBHP/Catalyst. To the mixture of two anthracenes (6.20×10^{-2} mmol of each) and standard (5.80×10^{-2} mmol) in 2.0 ml of benzene was added the appropriate catalyst (1% of $Rh(PPh_3)_3Cl$ or 2.5% of $VO(acac)_2$). A sample was withdrawn for GC analysis. After addition of TBHP in benzene (9.15×10^{-2} mmol for $Rh(PPh_3)_3Cl$ and 1.45×10^{-2} mmol for $VO(acac)_2$), the mixture was heated to 70° during 24 h. After cooling, the sample composition is analyzed by GC and the relative reactivities calculated as above [12].

Kinetic Measurements with Cr(VI). The anthracene (0.10 mmol) was dissolved by ultrasound in 100 ml of 95% AcOH, 8×10^{-4}N in H_2SO_4. Of this soln., 50 ml was thermostated to 25.0 ± 0.2° for 2 h. At t = O was added 2.5 ml of a freshly prepared 10^{-3}M Cr(VI) soln. (same solvent), and the soln. was quickly agitated. Samples of 1.0 ml were withdrawn at regular intervals by means of an *Eppendorf* pipette and quenched in a 25-ml volumetric flask containing 19 ml of H_2O, 2.5 ml 1N HCl, and 500 µl of 0.001M fresh solution of 1,5-diphenylcarbonohydrazide in 95% EtOH 0.027M in phthalic anhydride [11] [12] [32]. After 1.0 min, the flask was filled up to the mark with H_2O and 15 min later the soln. was filtered through a 8-µm disk into a 5-cm quartz cell. The optical density (A) of the Cr(VI)-1,5-diphenylcarbonohydrazide complex was measured at 540 nm (= 3.88×10^{-4} l·mol·cm^{-1}) by means of an *UVIKON 820* spectrophotometer.

Pseudo-first-order rate constants (k_{ps}) were obtained by linear regression with the equation:

$$\log A_t = \log A_o - \frac{k_{ps}}{2.303} \mathrm{x} t$$

and the second-order rate constats k_2 by dividing k_{ps} by the appropriate anthracene concentration [12]. For anthracenes carrying electron-attracting substituents plots of log A_t *vs.* t showed downward drifts. In these cases k_{ps} was obtained by extrapolation of the slope to t = O.

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