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# Liquid-Phase Oxidation of Deactivated Methylbenzenes by Aqueous Sodium Hypochlorite Catalyzed by Ruthenium Salts under Phase-Transfer Catalytic Conditions

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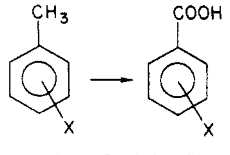
Toluene and methylbenzene ring substituted with electron-withdrawing substituents were oxidized to the corresponding carboxylic acids. The oxidation system is biphasic consisting of an organic substrate phase and an aqueous sodium hypochlorite phase with both ruthenium and quaternary ammonium salts acting as catalysts. Yields are essentially quantitative after 2 h at room temperature with a stoichiometric ratio hypochlorite/toluene of 4.5:1 provided the pH of the aqueous phase is between 8.0 and 10.5. Kinetic studies show the reaction to be of first order in the substrate, zero order in sodium hypochlorite, and combined first order in the catalysts. The reaction mechanism consists of a $RuO_4$-catalyzed hydride abstraction and a phase-transfer-catalyzed proton-dependent step.

The liquid-phase oxidation of ring-substituted methylbenzenes (toluenes) to the corresponding carboxylic acids is a widely performed reaction in the laboratory and industry. The oxidation may be effected by oxometal stoichiometric oxidants such as potassium permanganate ($KMnO_4$), potassium chromate ($K_2CrO_4$), or chromic acid ($H^+$, $CrO_3$).[1] Among non-oxometal oxidants nitric acid is commonly used.[2] In general all of the above reagents effectively oxidize methylbenzenes substituted by either electron-withdrawing or -donating groups. The major drawback of the oxometal oxidants is their relatively high price making them cost prohibitive on an industrial scale. Nitric acid oxidation is often problematic due to ring nitration; for example, oxidation of *o*-nitrotoluene yields picric acid and not the expected carboxylic acid.[3] Catalytic liquid-phase oxidations of toluenes are generally performed with molecular oxygen as primary oxidant and with catalytic amounts of cobalt acetate, manganese acetate, and bromide ions in acetic acid as solvent.[4] This oxidation is effective for activated aromatic compounds, e.g., toluene, *p*-xylene, or cresols, but extremely difficult (high pressure and temperature with low yields) for deactivated toluenes such as nitrotoluene.[5]

In this paper we present our results on the side chain oxidation of ring-deactivated methylbenzenes to the corresponding carboxylic acids in a two-phase (organic liquid/aqueous) system (eq 1). The oxidation of the organic substrate is effected by aqueous sodium hypochlorite as primary oxidant in the present of catalytic amounts of ruthenium tetraoxide ($RuO_4$), originally introduced as hydrated ruthenium trichloride ($RuCl_3{\cdot}3H_2O$), and quaternary ammonium phase-transfer catalysts. The use of ruthenium tetraoxide as a power oxidant is well-known to the organic chemist.[6] $RuO_4$ was first used stoichiometrically to oxidize phenanthrene to 9,10-phenanthrenequinone and sulfides to sulfones.[7] Later on acyclic and cyclic ethers were oxidized to esters and lactones, respectively,[8] and olefins were oxidatively cleaved to give ketones, aldehydes, and carboxylic acids.[9] Recently it was discovered that ruthenium tetraoxide can be used in catalytic amounts in the presence of various cooxidants. In acidic media common cooxidants are bromates, permanganates, lead tetracetate, and periodates, sodium periodate being most commonly used.[6] In alkaline media the generally used cooxidants are chlorine and hypochlorites. The combination ruthenium tetraoxide–sodium hypochlorite ($RuO_4$–NaOCl) was first used in the oxidation of olefins to carboxylic acids and ketones,[10-12] the oxidation of aromatic rings,[13,14] and the oxidation of alkynes.[15] More recently, it has been found that the $RuO_4$–NaOCl oxidation system could be improved by use of phase-transfer catalysis.[16,17] To date substituted methylbenzenes have only been oxidized to the respective carboxylic acids by using a ruthenium catalyst with sodium periodate[19] and phenyl iodosoacetate[20] as primary oxidants in an acidic homogeneous (acetic acid solvent) system. The use of a biphasic system with the inexpensive aqueous sodium hypochlorite as oxidant represents a unique, simple, and unusually mild technique for the oxidation of ring-deactivated methylbenzenes.



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## Results and Discussion

The side chain (methyl group) oxidation of ring-deactivated toluenes ($XC_6H_4CH_3$, X = H, Cl, Br, $NO_2$, CN) to the corresponding carboxylic acid is the subject of this paper. Attempted oxidation of such compounds by aqueous sodium hypochlorite solutions in a biphasic phase-transfer-catalyzed system along the lines previously

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**Table I. Oxidation of Methylbenzenes $XC_6H_4CH_3$ with $RuO_4$-NaOCl in a Biphasic Transfer-Catalyzed System**[a]

| substrate, X | product | yield,[b] % |
|---|---|---|
| *p*-$NO_2$ | carboxylic acid | 94 |
| *o*-$NO_2$ | carboxylic acid | 95 |
| *m*-$NO_2$ | carboxylic acid | 93 |
| *p*-Cl | carboxylic acid | 98 |
| *o*-Cl | carboxylic acid | 93 |
| *p*-Br | carboxylic acid | 95 |
| *o*-Br | carboxylic acid | 95 |
| *p*-ON | carboxylic acid | 97 |
| H | carboxylic acid | 92 |
| *p*-$OCH_3$ | ring + chlorinated compounds | 99[b] |
| *p*-OH | ring + chlorinated compounds | 98[c] |
| *p*-$CH_3$ | unidentified insoluble solid | 0[d] |

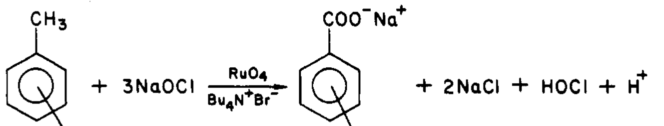
[a] Reaction conditions: 150 mL of 3 M NaOCl (0.45 mol); 0.1 mol of substrate, 0.005 mol of tetrabutylammonium bromide; 0.001 mol of $RuCl_3 \cdot 3H_2O$; 50 mL of dichloroethane (solvent); $T = 25$ °C; pH 9.0; stirring rate, 500 rpm; reaction time, 2 h. [b] Isolated yield—after phase separation, precipitation by acidification, filtration, and drying. [c] Yield by GC, less than ~1% carboxylic acid. [d] No *p*-toluic or terephthalic acid identified although the mixture is of organic nature.

**Table II. Observed First-Order Rate Constants as a Function of the Concentration of Aqueous Sodium Hypochlorite**[a]

| $k_{obsd}$, $s^{-1}$ | [NaOCl], M | $k_{obsd}$, $s^{-1}$ | [NaOCl], M |
|---|---|---|---|
| $6.10 \times 10^{-4}$ | 0.5 | $6.12 \times 10^{-4}$ | 2.6 |
| $6.20 \times 10^{-4}$ | 1.0 | $6.17 \times 10^{-4}$ | 3.0 |
| $6.07 \times 10^{-4}$ | 2.0 | $6.08 \times 10^{-4}$ | 3.2 |

[a] Reaction conditions: 0.60 mol of variable molar NaOCl (pH 9); 0.013 mol of *p*-chlorotoluene; 0.0013 mol of $Bu_4N^+Br^-$; 0.00013 mol of $RuCl_3 \cdot 3H_2O$; 24 mL of dichloroethane; $T = 25$ °C.

described for aromatic alcohols and aldehydes[21-23] were unsuccessful, yielding only recovered methylbenzenes, although such oxidations have been reported.[24] On the other hand, toluenes activated by electron-donating group ($ZC_6H_4CH_3$, Z = OH, $OCH_3$, $NH_2$, $OCH_2CH_3$) gave largely both ring- and α-chlorinated products in ratios depending on the pH of the sodium hypochlorite phase.[25] Only trace amounts of ruthenium trichloride could be detected. Addition of catalytic amounts of ruthenium trichloride had no effect on the product distribution in the case of ring-activated methylbenzenes. However, in the case of ring-deactivated toluenes quantitative yields of carboxylic acids were obtained. In Table I the results of the oxidation of various methylbenzens are summarized, showing the carboxylic acid products for the deactivated substrates and the chlorinated products for the activated substrates. The stoichiometric reaction equation may be written as in (for the deactivated substrates) eq 2.



(2)

From this stage on, we limit our discussion to ring-deactivated substrates. In this context it is important to emphasize several points. First, the ruthenium tetraoxide (formed in situ by the action of sodium hypochlorite on $RuCl_3$) is dissolved in the organic phase and is a necessary component in the reaction system. As long as sodium hypochlorite is present the organic phase retains a yellowish ($RuO_4$) color. Disappearance of the hypochlorite causes the immediate precipitation of black $RuO_2$, concluding the reaction. Second, the presence of a phase-transfer catalyst, quaternary ammonium salt, is also a necessary prerequisite for the reaction. In the absence of quaternary salt there is no reaction. Third, the pH of the sodium hypochlorite solution must be maintained between 8.0 and 10.5. At a pH below 8.0 the sodium hypochlorite solution is unstable and decomposes, preventing the desired reaction from taking place, whereas at pH's above 10.5 there is *no* reaction although the sodium hypochlorite solution is stable. Prior to adding the reaction substrate, the sodium hypochlorite is brought to pH 9 by addition of dilute sulfuric acid, and during the course of the reaction the acid formed is neutralized by pH-controlled addition of 20% aqueous NaOH. Ramifications of the above mentioned observations on the reaction mechanism will be discussed below.

**Kinetics.** In order to further understand the oxidation reaction kinetic studies were made in an attempt to clarify the reaction mechanism. To this end various aspects and parameters of the oxidation reaction were investigated in order to obtain a rate equation. First, the reaction order in the organic substrate was tested. Graphs of $-\ln(1 - x)$ where $x$ is the conversion vs. time gave linear plots indicating the reaction is of first order in the organic substrate. The observed rate constant, $k_{obsd}$, was found to be $6.17 \pm 0.05 \times 10^{-4}$ $s^{-1}$ under the given conditions (*p*-chlorotoluene was used as standard substrate with experimental conditions as in Table II using 3 M NaOCl). Further work to examine the effect of the hypochlorite solution concentration on the reaction rate showed that at various molar concentrations (from 0.5 to 3.2 M) the reaction rate was constant (Table II). The reaction is of zero order in sodium hypochlorite. The next step was to describe the influence of the concentration (amount) of the two catalysts on the reaction rate. One must note that it is difficult to know the organic phase concentration of the tetrabutyl ammonium bromide catalyst under the changing reaction conditions because the catalyst is partitioned between the organic and aqueous phases.[26] On the other hand, the $RuO_4$ catalyst is almost exclusively in the organic phase.[27] In Figure 1 one can see the effect of the initial Ru(III) concentration at a constant amount of $Bu_4N^+Br^-$ (10% mol of substrate) on the observed rate constant. Further analysis by a $\ln k_{obsd}$ vs. $\ln [RuO_4]$ plot shows that at low Ru(VIII) concentrations the reaction can be shown to be of first order in the metal catalyst, whereas at high concentrations the reaction order approaches zero. This indicates that there is a limit beyond which addition of more ruthenium salt has no effect on the reaction rate; the system is $RuO_4$ saturated. By performing experiments whereby the $RuO_4$ concentration is held constant and the amount of phase-transfer catalyst is changed (Figure 2), one can see this phenomenon in reverse. At low phase-transfer catalyst concentrations the reaction order approaches unity in the $Bu_4N^+Br^-$ catalyst as found by $\ln k_{obsd}$ vs. ln mol % $Bu_4N^+Br^-$ plots, whereas at high concentrations there is catalyst saturation, and the reaction order in the phase-transfer catalyst approaches zero. As

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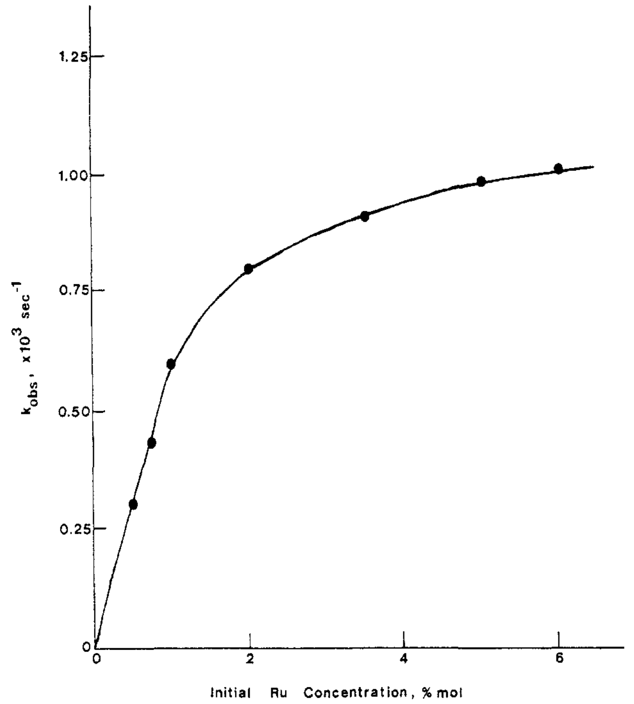


**Figure 1.** Observed first-order rate constant as a function of the initial ruthenium concentration. Reaction conditions: 0.60 mol of 3 M NaOCl (pH 9), 0.013 mol of *p*-chlorotoluene, 0.0013 mol of $Bu_4N^+Br^-$, variable amounts of $RuCl_3 \cdot 3H_2O$, 25 mL of dichloroethane, $T$ = 25 °C.

**Table III. The Effect of Various Substituents on the Reaction Rate**[a]

| substituent | $k_{obsd}$, min$^{-1}$ | substituent | $k_{obsd}$, min$^{-1}$ |
|---|---|---|---|
| *o*-$NO_2$ | 0.008 | *o*-Cl | 0.015 |
| *p*-$NO_2$ | 0.010 | *p*-Br | 0.035 |
| *p*-CN | 0.011 | *p*-Cl | 0.038 |
| *o*-Br | 0.016 | H | 0.037 |

[a] Reaction conditions: 0.6 mol of NaOCl (3 M, pH 9); 0.013 mol of substrate; 0.0013 mol of $Bu_4N^+Br^-$; 0.00013 mol of $RuCl_3 \cdot 3H_2O$; 25 mL of dichloroethane; $T$ = 25 °C.

a result of these kinetic experiments one may conclude that the reaction is of a combined first order in the two catalysts, the order for each catalyst being between zero and one depending on their relative concentrations.

The empiric kinetic rate law can therefore be summarized as being first order in the organic substrate, S, combined first order in the metal $RuO_4$ and $Bu_4N^+Br^-$ catalysts, and zero order in the sodium hypochlorite solution (eq 3). There remains the necessity in the context of the kinetic investigation to clarify two additional points. First the effect of various substituents on the reaction rate and second the presence of any intermediates or side products which may shed light on the reaction mechanism. The effect of various substituents on the reaction rate is summarized in Table III. One can see that as electron-withdrawing capability increases the reaction rate as presented by the observed first-order rate constant decreases. During the kinetic experiments which were followed by GLC no possible or probable intermediates such as benzyl alcohols or benzaldehydes were detected. This indicates that if such compounds are formed they react immediately. On the other hand in certain cases trace (~2%) amounts of benzyl benzoate ester were detected.

$$r = k[S][RuO_4]^{0\to 1}[Bu_4N^+Br^-]^{1\to 0} \qquad (3)$$

**Mechanism.** From the data described above certain mechanistic conclusions will be drawn and guidelines for a mechanism given. In general, the reaction from the toluene to carboxylic acid may be expectd to proceed through an alcohol and/or aldehyde intermediate. The absence of detectable intermediates indicates that the first stage of toluene oxidation is rate-determining and the reaction may thus be presented as in eq 4. Control experiments with benzyl alcohols and benzyl aldehydes as substrates also gave benzoic acids. Additional evidence indicating an alcoholic intermediate can be shown from the fact that benzyl benzoate is sometimes a reaction byproduct. We have shown in the past that the oxidation of benzyl alcohols by NaOCl/PTC systems give esters as products under certain conditions.[23]

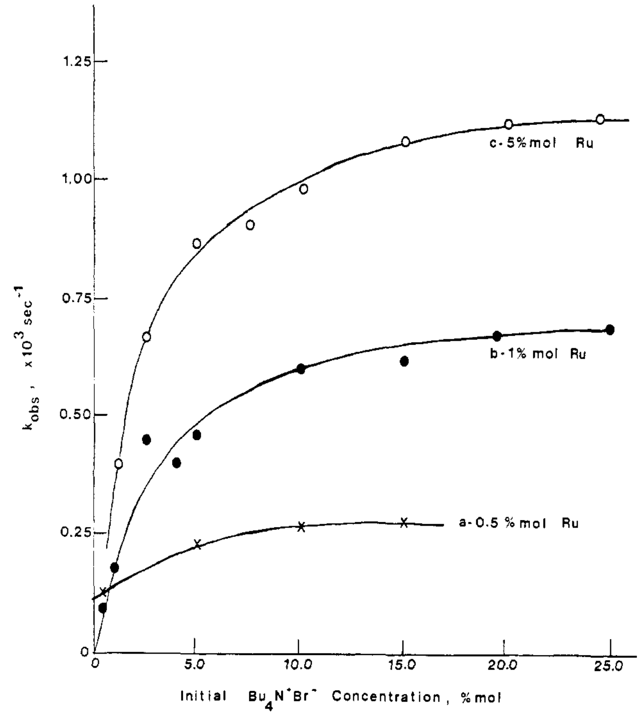
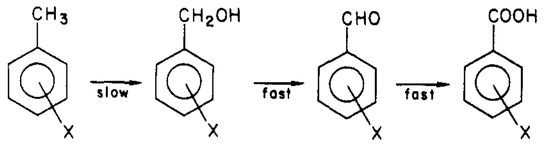


**Figure 2.** Observed first-order rate constant as a function of the amount of tetrabutylammonium bromide. Reaction conditions: 0.60 mol of 3 M NaOCl (pH 9), 0.013 mol of *p*-chlorotoluene, 0.000065 mol of 0.5 mol % $RuCl_3 \cdot 3H_2O$ (curve a), 0.00013 mol of 1.0 mol % $RuCl_3 \cdot 2H_2O$ (curve b), or 0.00065 mol of 5 mol % $RuCl_3 \cdot 3H_2O$ (curve c), variable amounts of $Bu_4N^+Br^-$, 25 mL of dichloroethane, $T$ = 25 °C.



(4)

In the past it has been shown in acidic homogenous systems that the formation of a carbonium ion by hydride abstraction is the rate-determining step in the oxidation reaction.[28,29] Since strongly electron-withdrawing substituents on the aromatic ring decrease the reaction rate (Table III) a mechanism whereby a carbonium ion is formed in the rate-determining step is also likely in this case eq 5. In eq 5, the second stage is fast; however, our results indicate other possibilities.

Equation 5 indicates that the reaction should be first order in $RuO_4$ and substrate. However, we have found not only that the phase-transfer catalyst is an essential component in the oxidation system but that the reaction is of

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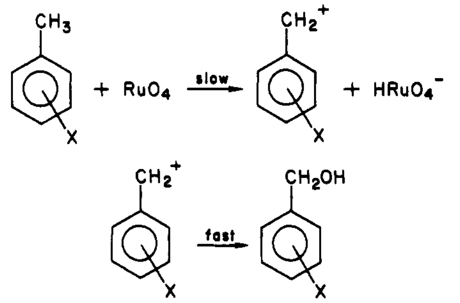

(5)

variable order in the phase-transfer catalyst. This indicates that the catalyst may be involved in the rate-determining step of the mechanism. The need for a phase-transfer catalyst cannot be explained vis-â-vis a function for reoxidizing the reduced ruthenium catalyst for this oxidation takes place in the absence of a phase transfer catalyst.[10-14] Furthermore, the reaction only proceeds at a pH between 8.0 and 10.5 preferably at 9.0 in the aqueous phase. It has been shown in the past[22] that at these pH's the hypochlorite ion is extracted into the organic phase as in eq 6.

$$\mathrm{Bu_4N^+Br^-(org) + NaOCl(aq) \rightarrow Bu_4N^+OCl^-(org) + NaBr(aq)} \quad (6)$$

$$\mathrm{Bu_4H^+OCl^-(org)} + n\mathrm{HOCl(aq) \rightarrow Bu_4N^+OCl^-\cdots HOCl}_n\mathrm{(org)}$$

Under these conditions both the hypochlorite anion and the hypochlorous acid are extracted. At a pH above 10.5 only hypochlorite anion is present in the aqueous phase ($\mathrm{p}K_a$(HOCl) 7.53), and therefore only the anion is extracted.

A complete mechanism for the oxidation of methylbenzene under the given conditions must not only take into account the hydride abstraction by $RuO_4$, forming the carbonium ion as indicated in eq 5, but must also take into account the function of the phase-transfer catalyst, which transfers protons and hypochlorite anions into the organic phase. A complete mechanistic scheme will therefore include a hydride-abstraction step and at least another intermediate reaction step that is most likely proton or pH dependent. The relative concentrations of the catalysts will determine the effect of each stage in the rate equation.

## Experimental Section

**General Procedure for Preparation of Carboxylic Acids.** In a 250-mL reactor equipped with a heating jacket were placed 150 mL of 3 M NaOCl, 0.10 mol of methylbenzene, 5 mol % tetrabutyl ammonium bromide, 1 mol % $RuCl_3 \cdot 3H_2O$, and 50 mL of dichloroethane. The pH at the aqueous phase was brought to pH 9 ± 0.1 by addition of 20% v/v $H_2SO_4$. Stirring was commenced with a Heidolph RZR-1 mechanical stirrer at 500 rpm and the temperature held at 25 ± 1 °C. The pH was controlled during the reaction by using an El-Hamma APC-616 pH controller coupled to a peristaltic pump Ismatec IP-4 which fed 20% of NaOH to keep the pH at 9 ± 0.1. About 0.2 mol of NaOH is added during the reaction period of 2 h. After the hypochlorite solution was used up ($RuO_2$ precipitates out) a few drops of hypochlorite solution were added to reoxidize the ruthenium catalyst. The phases were separated and the aqueous phase is acidified with dilute 20% $H_2SO_4$. The carboxylic acid immediately precipitated and was filtered, washed, and dried, giving a 90–98% yield.

**Kinetic Experiments.** In a 250-mL reaction equipped with a heating jacket and a pH controller coupled to a peristaltic pump with a 20% NaOH feed (described above) were placed 200 mL of 3 M NaOCl (0.60 mol) at pH 9 ± 0.1, 0.013 mol of *p*-chlorotoluene in 25 mL of dichloroethane solvent. At the start of the reaction after equilibration of the temperature at 25 ± 0.5 °C, 0.0013 mol of $Bu_4N^+Br^-$ and 0.00013 mol of $RuCl_3 \cdot 3H_2O$ were added. A 0.25-mL aliquot of the organic phase was taken every 10 min, and the disappearance of the substrate was followed by GLC using the solvent as internal standard. Analyses were made with a Varian 3700 gas chromatograph equipped with a FID detector. The column used was a 2-m 3% OV-17 on 80–100 mesh Chromasorb W acid washed at an initial temperature of 80 °C for 1 min, a rise rate of 20 °C/min, and a final temperature of 280 °C under a $N_2$ flow of 20 $cm^{-3}$/min.

## Conclusion

In this paper a novel method for oxidizing ring-deactivated methylbenzenes to carboxylic acids has been described. The oxidation system is a biphasic reaction whereby an aqueous solution of sodium hypochlorite is the primary oxidant with ruthenium and quaternary ammonium salts as catalysts. The reaction was found to be effective for all deactivated methylbenzenes with high hypochlorite yields at ambient temperatures, provided the pH of the aqueous phase is between 8.0 and 10.5, preferably 9.0. Kinetic studies show the reaction to be first order in the organic substrate, zero order in the hypochlorite solution, and combined first order in the two catalysts. The reaction mechanism probably consists of a hydride-abstraction step catalyzed by $RuO_4$ and a proton-dependent step catalyzed by the phase-transfer catalyst.

**Registry No.** *p*-$CH_3C_6H_4NO_2$, 99-99-0; *o*-$CH_3C_6H_4NO_2$, 88-72-2; *m*-$CH_3C_6H_4NO_2$, 99-08-1; *p*-$CH_3C_6H_4Cl$, 106-43-4; *o*-$CH_3C_6H_4Cl$, 95-49-8; *p*-$CH_3C_6H_4Br$, 106-38-7; *o*-$CH_3C_6H_4Br$, 95-46-5; *p*-$CH_3C_6H_4CN$, 104-85-8; $CH_3C_6H_5$, 108-88-3; *p*-$HO_2CC_6H_4NO_2$, 62-23-7; *o*-$HO_2CC_6H_4NO_2$, 552-16-9; *m*-$HO_2CC_6H_4NO_2$, 121-92-6; *p*-$HO_2CC_6H_4Cl$, 74-11-3; *o*-$HO_2CC_6H_4Cl$, 118-91-2; *p*-$HO_2CC_6H_4Br$, 586-76-5; *o*-$HO_2CC_6H_4Br$, 88-65-3; *p*-$HO_2CC_6H_4CN$, 619-65-8; $HO_2CC_6H_5$, 65-85-0; *p*-$CH_3C_6H_4OCH_3$, 104-93-8; *p*-$CH_3C_6H_4OH$, 106-44-5; *p*-$CH_3C_6H_4NH_2$, 106-49-0.