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A Set of Rate Constants for the Reactions of OH Radicals with Aromatic Hydrocarbons

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Synopsis. The rate constants for the reactions of OH radicals with seventeen aromatic hydrocarbons were determined at atmospheric pressure and room temperature from competitive reactions with hexane, using H_2O_2 as the OH-radical source. A useful trend was found in the structure-reactivity relationship.

Since aromatic hydrocarbons are important constituents of polluted urban air, and since they are believed to be consumed mainly by reactions with OH radicals, several papers have been published on the rate constants for the reactions of OH radicals with aromatic hydrocarbons.[1,2] Besides absolute rate constants determined by sophisticated techniques, relative rate constants determined by competitive reactions between aromatic hydrocarbons and a certain reference compound at atmospheric pressure and room temperature have been reported.[3,4] They used NO_x as a source of OH radicals, but we have proposed a different and simpler method to produce OH from the photolysis of hydrogen peroxide (H_2O_2, 90%) at 2537 A to obtain the rate constants for the reaction of OH with atmospheric elements of interest and have reported some empirical relationships between the reactivity towards OH and the structures of the olefins.[5,6] We here try to apply the method to aromatic hydrocarbons, using hexane as a reference compound, and propose a set of rate constants for the reactions of OH with a series of aromatic hydrocarbons; further, we try to find a useful trend in the reactivity-structure relationship.

The experimental procedure and data treatment were similar to those described in previous works.[5,6] Plots of $\ln([\text{aromatic}]_0/[\text{aromatic}]_t)$ against $\ln([\text{hexane}]_0/[\text{hexane}]_t)$ were on excellent straight lines for any compound; the slopes show the relative rate constants of aromatics to hexane. At least ten runs were carried out to determine the relative rate constants. The rate constants did not show any dependence on the variation in the initial concentrations of the reactants. Since methoxybenzene was photolyzed by the irradiation at 2537 A, methyl nitrite prepared by ourselves was used as another OH radical source by irradiating it in a mixture of reactants and oxygen at 360 nm.[7] No decomposition of other aromatics was observed because of short-time, weak irradiation.

A set of rate constants for the reactions of OH radicals with aromatic hydrocarbons is shown in Table 1, along with the literature data. The error limits in the table are the standard deviations for repeated runs. Most of the rate constants determined in this work showed fairy good agreement with literature values determined by completely different methods. For the compounds

TABLE 1. ROOM-TEMPERATURE RATE CONSTANTS FOR THE REACTIONS OF AROMATIC HYDROCARBONS WITH OH RADICALS

Aromatic	Rate constant Relative to k_{hexane}	 Absolute[a)] $\times10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Reference[b)]
Benzene	0.26±0.01	1.53±0.06	1.59±0.12[8], 1.24±0.12[9], 1.20±0.15[10], 1.21±0.09[11]
Toluene	1.08±0.03	6.37±0.08	6.11±0.40[8], 3.9±1.7[3], 5.78±0.58[9], 5.78±0.58[9], 6.40±0.64[10], 6.36±0.69[11]
Ethylbenzene	1.16±0.05	6.84±0.30	7.5±1.5[4], 7.95±0.50[12]
Isopropylbenezene	1.12±0.06	6.61±0.30	5.7±1.1[4], 7.79±0.50[12]
Propylbenzene	1.18±0.04	6.94±0.24	5.8±1.2[4], 5.86±0.50[12]
t-Butylbenzene	0.82±0.08	4.84±0.47	
O-Xylene	2.24±0.10	13.2±0.6	12.0±3.6[3], 15.3±1.5[9], 14.3±1.5[10], 12.4±1.2[10], 14.2±1.7[13]
2-Ethyltoluene	2.23±0.22	13.2±1.3	12.9±2.6[4]
M-Xylene	3.97±0.11	23.4±0.7	21.0±1.4[3], 23.6±2.4[9], 20.2±4.0[4], 24.0±2.5[10], 20.6±1.3[12]
3-Ethyltoluene	3.80±0.18	22.4±1.1	18.3±3.7[4]
P-Xylene	2.31±0.10	13.6±0.6	11.5±2.5[3], 12.2±1.2[9], 15.3±1.7[10], 10.5±1.0[12], 13.5±1.4[13]
4-Ethyltoluene	2.30±0.22	13.6±1.3	12.2±2.4[4]
1,2,3-Trimethylbenzene	5.30±0.73	31.3±4.3	21.3±4.5[3], 26.4±2.6[9], 33.3±4.5[10]
1,2,4-Trimethylbenzene	5.65±0.22	33.3±1.3	30.8±5.6[3], 33.5±3.4[9], 40.0±4.5[10]
1,3,5-Trimethylbenzene	6.94±0.94	40.9±5.6	62.4±7.5[10]
Fluorobenzene	0.16±0.02	0.87±0.03	
Methoxybenzene	2.52±0.10	14.9±0.6	19.6±2.4[14]

a) Absolute rate constants were derived using a rate constant for the reaction of OH with hexane of $5.9\times10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$, the mean of three values in Ref. 1). b) Numbers in bracket indicate references.

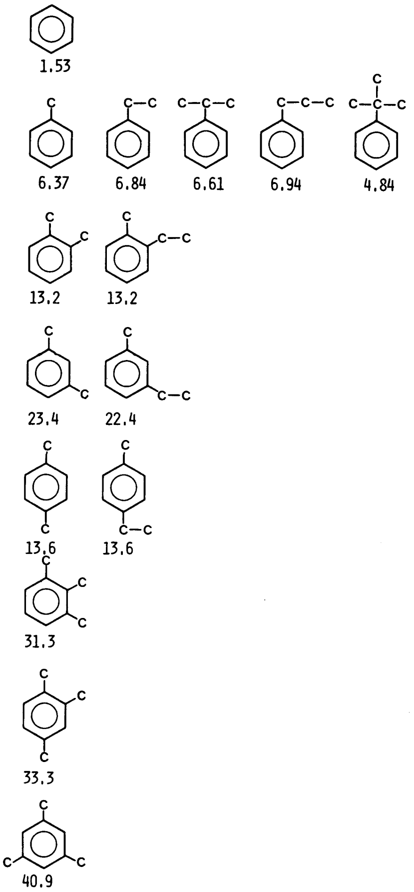

Fig. 1. Reactivity-structure relationship of aromatic hydrocarbons towards OH radicals. (all units in 10^{-12} cm^3 $molecule^{-1}$ s^{-1}).

whose literature values are diverse, our values generally agreed with the most recent values.

Since the set of rate constants for the series of aromatics was obtained under the same experimental conditions and using the same reference compound, it is possible for us to compare the rate constants one by one. Figure 1 shows the aromatic hydrocarbons classified by the positions and length of the substituents, along with the obtained rate constants in this work. It was confirmed that the OH-radical rate constants at room temperature increase as the degree of alkyl substitution increases, showing the same trend of degree and position of alkylation as in $O(^3P)$-atom reactions.[14)] This implies that the major reaction path is the electrophilic addition of OH radicals to aromatic rings.

Furthermore, we notice that an empirical rule was derived from Fig. 1. The replacement of the methyl group on the aromatic ring by a longer alkyl chain (C_2, C_3) will not much affect the reactivity of methyl-substituted aromatics; the rate constants for aromatics on the same row in Fig. 1 are almost equal to each other except for *t*-butylbenzene in the row of toluene derivatives. There has been some uncertainty as to the branching ratio for the abstraction of methyl-H to the overall reaction in the reaction of toluene with OH radicals. The most recent work of Atkinson *et al.*[15)] indicates that, at 300 K, the branching ratio is 0.08 ± 0.03; however, the reported values have varied from 0.16,[10)] 0.15 ± 0.02,[16)] to 0.1—0.02 (most probably 0.04).[11)] The finding that toluene, ethylbenzene, isopropyl- and propylbenzenes have almost identical rate constants supports the lower value of the branching ratio of abstraction, because the loss of reactive methyl-H in toluene by replacement with methyl group (s) did not make the rate constant for unsubstituted toluene decrease significantly. *t*-Butylbenzene, apart from the four homologs, showed a smaller rate constant. The steric hindrance of the *t*-butyl group for the OH radical attack at the ortho position may explain it.

The trend found in this work is useful in getting an overall understanding of the reactivity of a series of aromatic hydrocarbons towards OH radicals and in evaluating the rate constants reported separately.

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