PERGAMON

Chemosphere 53 (2003) 1–7

CHEMOSPHERE

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Competition kinetics using the UV/H_2O_2 process: a structure reactivity correlation for the rate constants of hydroxyl radicals toward nitroaromatic compounds

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Received 28 October 2002; received in revised form 11 February 2003; accepted 31 March 2003

Abstract

The rate constants for hydroxyl radical reaction toward a set of nitroaromatic substrates k_S, have been measured at 25 °C using competition experiments in the UV/H_2O_2 process. For a given pair of substrates S_1 and S_2, the relative reactivity β (defined as k_{S1}/k_{S2}) was calculated from the slope of the corresponding double logarithmic plot, i.e., of ln[S_1] vs. ln[S_2]. This method is more accurate and remained linear for larger conversions in comparison with the plots of ln[S_1] and ln[S_2] against time. The rate constants measured ranged from 0.33 to 8.6×10^9 $M^{-1}\,s^{-1}$. A quantitative structure–reactivity relationship was found using the Hammett equation. Assuming σ values to be additive, a value of −0.60 was obtained for the reaction constant ρ. This value agrees with the high reactivity and the electrophilic nature of HO· radical.

Keywords: Advanced oxidation processes; Nitroaromatic compounds; Hydroxyl radical; Competitive kinetics; Hammett equation

1. Introduction

Various advanced oxidation processes (AOPs) are nowadays available and applicable at laboratory, pilot or even technical levels for achieving oxidative degradation of organic pollutants in aqueous media (Legrini et al., 1993; Fujishima et al., 2000; Lopez et al., 2000). Most of these processes are based on the production of hydroxyl radicals as primary oxidizing species. The reaction of hydroxyl radicals with organic compounds (by addition to double bonds and/or by hydrogen abstraction) generates C-centered organic radicals that are subsequently trapped by dissolved molecular oxygen to yield peroxides and peroxyl radicals (Getoff, 1997; Von Sonntag et al., 1997).

UV/H_2O_2 oxidation technology is frequently employed for degradation of pollutants in wastewater (Ho, 1986; Juang et al., 1997; Carter et al., 2000). It has been recognized that the efficiency of the oxidation process strongly depends on experimental conditions (Shu et al., 1994; Stefan et al., 1996; Poon et al., 1999; Lopez et al., 2000; Wang et al., 2000; García Einschlag et al., 2002a,b). For practical application an understanding of the photo-degradation mechanism is very important to achieve improvements in the yield and the efficiency of these processes.

A detailed kinetic modeling of the AOP requires the knowledge of the degradation pathways, as well as the rate constants for the reaction of hydroxyl radical with the primary pollutant (k_S) and all the degradation intermediates (Glaze et al., 1995; Stefan et al., 1996; Stefan and Bolton, 1998; Crittenden et al., 1999). We have

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doi:10.1016/S0045-6535(03)00388-6

recently shown that, the efficiency of the UV/H_2O_2 process for the oxidation of nitroaromatic compounds can be analyzed using a very simple approach (Lopez et al., 2000; García Einschlag et al., 2002a,b). The proposed model is a potential tool for the study of basic and applied processes of interest in environmental chemistry. The equations we reported show that one of the parameters that govern the kinetic behavior of the oxidation process is the rate constant for the reaction of hydroxyl radicals with the nitroaromatic compounds. Thus, the knowledge of k_S is very important for predicting the best operating conditions to achieve an optimal efficiency of the UV/H_2O_2 method.

The measurement of absolute rate constants for the reactions of $HO^{\cdot}$ with organic compounds is a difficult task frequently carried out by pulse radiolysis studies with fast spectroscopic analysis of transient growth or decay (Neta and Dorfman, 1968; Ashton et al., 1995). However, an evaluation of these rate constants can be easily performed by competition experiments where a given substrate competes for $HO^{\cdot}$ radicals with a reference compound whose reactivity towards $HO^{\cdot}$ is already known (Kochany and Bolton, 1991; Onstein et al., 1999; Pignatello et al., 1999).

In the present communication we analyze the reactivity of hydroxyl radical with a series of nitroaromatic compounds based on a competition kinetics scheme using the UV/H_2O_2 technique. Rate constant values for hydroxyl radicals with the substrates 4-chloro-3,5-dinitrobenzoic acid (CDNBA), 1-chloro-2,4-dinitrobenzene (CDNB), 1,3-dinitrobenzene (DNB), 2,4-dinitrophenol (DNP), nitrobenzene (NBE), 3-nitrophenol (MNP), 2-nitrophenol (ONP), 4-nitrophenol (PNP), 3-nitrotoluene (MNT) and 4-nitrotoluene (PNT) were obtained from competitive experiments. The trend observed for the rate constants with the electron withdrawing ability of the substituents in the aromatic ring is discussed in terms of a Hammett correlation.

2. Materials and methods

2.1. Chemicals

CDNBA (97%, Aldrich) was previously purified as already described (Lopez et al., 2000). CDNB (99%, Aldrich), DNB (98%, Fluka), DNP (99%, Riedel-deHaën), NBE (95%, May&Baker), MNP (98%, Riedel-deHaën), ONP (98%, Riedel-deHaën), PNP (99% Fluka; 98%, Riedel-deHaën), MNT (99%, Riedel-deHaën), PNT (98%, Fluka) were used without further purification. Aqueous solutions containing 50–100 $\mathrm{mg\,l^{-1}}$ of substrate were used. The initial pH was adjusted to 2.5 using H_2SO_4 (Merck). Dissolution of the organic compounds was facilitated by sonication (when required, solutions were cooled in order to avoid heating induced by ultrasonic waves). Concentrations of H_2O_2 (30% Perhydrol, Merck) ranged from 1.0×10^{-2} to 0.1 M. Water was of Milli-Q quality. All other chemicals used were ACS grade. H_2O_2 (30% w/w in H_2O), H_2SO_4, H_3PO_4, $KMnO_4$, triethanolamine (TEA), and acetonitrile were purchased from Merck. H_2O_2 was analyzed by the classical $KMnO_4$-titration method.

2.2. Absorbance measurements

Absorption spectra were registered on a double beam Cary 3 spectrophotometer. Measurements were made using quartz cells of 0.2 cm optical path length.

2.3. HPLC measurements

HPLC analyses were carried out with a HPLC Konic 500 B equipment with a Spherisorb S5 ODS2 (250 × 46 mm) column and a Lambda Bischoff 1000 spectrophotometer as detection system. The wavelength of analysis was set to 275 nm. The eluent was a mixture of acetonitrile and water (40/60). The aqueous phase contained 2 ml TEA and 1.2 ml H_3PO_4 dissolved in 1 l water. A flow rate of 1 ml/min was used. Calibration curves for all substrates were obtained under identical conditions.

2.4. Photochemical reactor

The experiments were performed in an annular photochemical reactor (Nr 1326, DEMA, Mangels, Bornheim-Roisdorf, Germany). The reactor had a volume of 750 ml (internal radius = 2.0 cm, external radius = 4.0 cm and height = 20.0 cm), and was equipped with a medium pressure Hg arc (Philips HPK 125 W), positioned in the axis of the reactor in a well made of quartz. The spectral distribution of the emission of this lamp has been published elsewhere (García Einschlag et al., 2002b). The photon flow entering the reactor was 1.3×10^{-5} $\mathrm{einsteins\,s^{-1}\,l^{-1}}$ in the wavelength range 200–450 nm, as estimated from potassium ferrioxalate actinometry (Braun et al., 1991) and the spectral emission profile of the lamp. The reactor was equipped with ports for sample withdrawing. The purging gas was introduced from below through a glass frit. Solutions were continuously purged with synthetic air (21% O_2 in N_2) and the temperature maintained at 25 °C (±1 °C). H_2O_2 was added to the reaction system just before starting the irradiation.

2.5. Competition kinetics and the UV/H_2O_2 process

Competition kinetics is used to compare the reactivities of solutes present together in the same solution and, thus, under absolutely identical conditions. A system where UV radiation is applied to a solution containing two organic substrates (S_1 and S_2) and H_2O_2 can be described by the following set of rate-limiting reaction steps (Onstein et al., 1999; Carter et al., 2000; Lopez et al., 2000; García Einschlag et al., 2002a,b):

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad P_{HP}\cdot\Phi_{HP} \tag{A}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad k_{HP} \tag{B}$$

$$HO^{\bullet} + S_1 \rightarrow \text{Products} \quad k_{S1} \tag{C}$$

$$HO^{\bullet} + S_2 \rightarrow \text{Products} \quad k_{S2} \tag{D}$$

$$HO^{\bullet} + IP \rightarrow \text{Products} \quad k_{IP} \tag{E}$$

Here IP represents the set of intermediate products that consume $HO^{\bullet}$ radicals through secondary reactions.

In the previous scheme the degradation of the substrates by secondary reactions ($HO_2^{\bullet}$ radicals are much less reactive than $HO^{\bullet}$ radicals) and phototolysis were not considered. The first assumption is valid for small conversions where the buildup of secondary oxidants, able to initiate alternative degradation pathways, is not significant. The second assumption holds for either high concentrations of hydrogen peroxide (since practically all the radiation is absorbed by H_2O_2) or very small quantum efficiencies of UV photolysis η_S. Except for PNT and MNT, η_S of the other studied nitroaromatic compounds have been determined to be between 10^{-3} and 10^{-5} (Simmons and Zepp, 1986; García Einschlag et al., 2002b). The reported quantum yields at 366 nm for PNT and MNT are, 5.2×10^{-3} and 2.1×10^{-2}, respectively (Simmons and Zepp, 1986).

Since bimolecular reactions C and D are rate-limiting steps, the rate laws of S_1 and S_2 depletion are:

$$\frac{-d[S_1]}{dt} = k_{S1}[HO^{\bullet}][S_1] \Rightarrow \frac{d\ln[S_1]}{dt} = -k_{S1}[HO^{\bullet}] \tag{1a, 1b}$$

$$\frac{-d[S_2]}{dt} = k_{S2}[HO^{\bullet}][S_2] \Rightarrow \frac{d\ln[S_2]}{dt} = -k_{S2}[HO^{\bullet}] \tag{2a, 2b}$$

Combining Eqs. (1) and (2) the relative reactivity β, defined as k_{S1}/k_{S2}, can be obtained from the experimental behavior of $\ln[S_1]$ and $\ln[S_2]$. If the absolute rate constant k_{S2} is known and the β value is experimentally measured, the absolute rate constant for S_1 can be calculated using k_{S2} as reference value (i.e., $k_{S1} = \beta \cdot k_{S2}$). Two different methods have been applied to obtain β values (Onstein et al., 1999; Pignatello et al., 1999).

2.5.1. Method I

If the steady-state condition is assumed for hydroxyl radicals, it can be shown that $HO^{\bullet}$ concentration is given by

$$[HO^{\bullet}]_{SS} = \frac{P_{HP}\cdot\Phi_{HO}}{k_{S1}[S_1] + k_{S2}[S_2] + k_{IP}[IP] + k_{HP}[H_2O_2]} \tag{3}$$

where P_{HP} (in einsteins $s^{-1}\,l^{-1}$) is the number of photons absorbed by H_2O_2 per unit time and unit volume, and $\Phi_{HO^{\bullet}}$ the quantum efficiency of hydroxyl radicals production. The numerator in Eq. (3) represents the rate of $HO^{\bullet}$ production, while the terms in the denominator represent the depletion paths of $HO^{\bullet}$. As long as the initial concentration of H_2O_2 is large and the initial concentrations of the substrates and the intermediate products are small enough so that $k_{HP}[H_2O_2] \gg (k_{S1}[S_1] + k_{S2}[S_2] + k_{IP}[IP])$ during the experimental run, both S_1 and S_2 will exhibit pseudo-first-order decays:

$$\ln\frac{[S_1]_t}{[S_1]_0} = -k_{S1}[HO^{\bullet}]_{SS}t \Rightarrow \ln\frac{[S_1]_t}{[S_1]_0} = -k'_{S1}t \tag{4a, 4b}$$

$$\ln\frac{[S_2]_t}{[S_2]_0} = -k_{S2}[HO^{\bullet}]_{SS}t \Rightarrow \ln\frac{[S_2]_t}{[S_2]_0} = -k'_{S2}t \tag{5a, 5b}$$

where k'_{S1} and k'_{S2} are pseudo-first-order rate constants (i.e., $k'_{S1} = k_{S1}\cdot[HO^{\bullet}]_{SS}$ and $k'_{S2} = k_{S2}\cdot[HO^{\bullet}]_{SS}$), calculated from the linear plots of $\ln[S_1]$ and $\ln[S_2]$ vs. *time*. Under these conditions, the relative reactivity is given by the ratio of the apparent rate constants:

$$\beta = \frac{k'_{S1}}{k'_{S2}} \tag{6}$$

2.5.2. Method II

If no assumption for the time dependence of the concentration profile for hydroxyl radicals is made, integration of expressions (1b) and (2b) yields

$$-\ln\frac{[S_1]_t}{[S_1]_0} = k_{S1}\int_0^t [HO^{\bullet}]\,dt \tag{7}$$

$$-\ln\frac{[S_2]_t}{[S_2]_0} = k_{S2}\int_0^t [HO^{\bullet}]\,dt \tag{8}$$

From Eqs. (7) and (8), β is given by Eq. (9):

$$\beta = \frac{\ln([S_1]_t/[S_1]_0)}{\ln([S_2]_t/[S_2]_0)} \tag{9}$$

Hence the desired ratio of the rate constants can be obtained from the plot of $\ln[S_1]$ vs. $\ln[S_2]$. It is worth to mention that Eq. (9) holds even if $[HO^{\bullet}]$ changes with time.

3. Results and discussion

3.1. Rate constant measurements

Competition experiments among different pairs of the investigated substrates were carried out in order to determine β values for relative rate constants.

Time-resolved spectra were recorded and the concentration profiles were followed using HPLC analysis.

Fig. 1 shows the kinetic profiles obtained for the couple DNP–CDNB. It can be observed that both substrates follow first-order kinetics, as predicted by Eqs. (4b) and (5b). The experimental slopes are $(2.80 \pm 0.09) \times 10^{-2}$ s^{-1} and $(1.05 \pm 0.03) \times 10^{-2}$ s^{-1} for DNP and CDNB, respectively. By introducing these results in Eq. (6) a value of 2.67 ± 0.11 for β was obtained.

Fig. 2 shows the behavior of ln[DNP] vs. ln[CDNB]. The linear plot predicted by Eq. (9) yielded a value of 2.74 ± 0.07.

The comparison of the results presented in Figs. 1 and 2 shows that, within experimental error, both methods give the same β values. However, for all the couples of substrates studied, the double logarithmic plots remained linear for larger degree of conversions (i.e., since the integrals of Eqs. (7) and (8) are identical, Eq. (9) is valid even if [HO·] is time dependent) and the estimated standard errors were smaller.

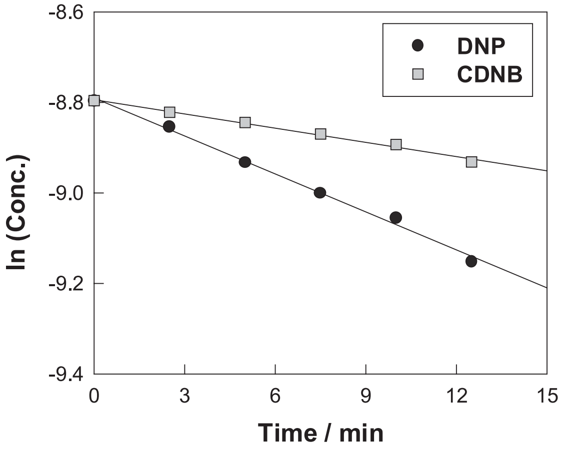

Fig. 1. Competitive kinetic profiles obtained for the couple DNP–CDNB. $[DNP]_0 = 7.2 \times 10^{-4}$ M, $[CDNB]_0 = 7.2 \times 10^{-4}$ M, $[H_2O_2]_0 = 5.0 \times 10^{-2}$ M.

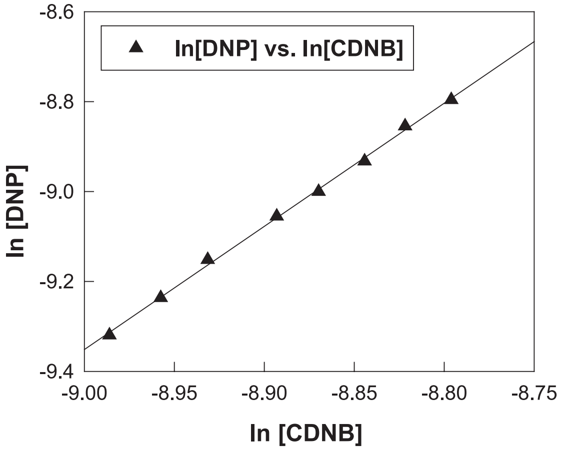

Fig. 2. Double logarithmic plot involving DNP and CDNB. $[DNP]_0 = 7.2 \times 10^{-4}$ M, $[CDNB]_0 = 7.2 \times 10^{-4}$ M, $[H_2O_2]_0 = 5.0 \times 10^{-2}$ M.

Table 1
Relative rate constants (β) for the reaction for HO· radicals with different couples of nitroaromatic compounds

Substrate couple	β
ONP/PNP	0.95 ± 0.1
DNB/CDNB	1.4 ± 0.1
PNP/NBE	1.5 ± 0.2
PNT/NBE	2.0 ± 0.2
MNT/NBE	2.1 ± 0.2
DNP/CDNB	2.7 ± 0.1
CDNB/CDNBA	2.8 ± 0.2
NBE/CDNB	5.4 ± 0.7
MNP/CDNB	6.1 ± 0.7
DNP/CDNBA	7.5 ± 0.5
PNP/CDNB	8.0 ± 1.0
NBE/CDNBA	12.1 ± 2
PNP/CDNBA	18.5 ± 3

The indicated error values correspond to one standard deviation.

The relative rate constant values obtained, applying Eq. (9) to all the competition experiments performed, are listed in Table 1.

In spite of some dispersion, the values of Table 1 show that the reactivity order of the different substrates analyzed towards HO· radicals is the following one: MNT > PNT > PNP > ONP > MNP > NBE > DNP > DNB > CDNB > CDNBA. Similar trends on reactivity were also observed in the photocatalytic degradation of related nitroaromatic compounds (Dillert et al., 1995).

It is worth noting that, in general, for β values larger than 10 (or smaller than 0.1) the estimated dispersion is higher than 15%. If one of the compounds is much more reactive, the slope of the less reactive compound will have a large relative error due to the small change in concentration. Hence, to avoid high experimental errors in competition experiments, the substrate and the compound used as reference should have comparable reactivities.

From the experimental β values, absolute rate constants can be calculated using NBE as the reference compound, $k_{NBE} = 4.2 \times 10^9$ $M^{-1}\,s^{-1}$ at 298 K (Ashton et al., 1995). Since several couples of substrates were used, some constants can be calculated using more than one experimental β value. In order to obtain the best set of rate constants that, in a least-squares sense, fits the experimental β values of Table 1, a software program was specially developed in our laboratory. The results obtained are presented in Table 2.

Table 2
Rate constants for the investigated nitroaromatic substrates with HO· radicals obtained in this work (pH = 2.5 and $t = 25$ °C)

Substrate	k_S/M^{-1} s^{-1} (this work)	k_S/M^{-1} s^{-1} (literature data)
CDNBA	$(3.3 \pm 0.2) \times 10^8$	3.5×10^8[a]
CDNB	$(8.2 \pm 0.5) \times 10^8$	8.7×10^8[b]
DNB	$(1.1 \pm 0.5) \times 10^9$	–
DNP	$(2.3 \pm 0.4) \times 10^9$	5.7×10^9[c]
NBE	$(4.2 \pm 0.4) \times 10^9$	4.7×10^9[d]
MNP	$(5.0 \pm 0.4) \times 10^9$	7.1×10^9[e]
ONP	$(5.9 \pm 0.7) \times 10^9$	9.2×10^9[e]
PNP	$(6.2 \pm 0.6) \times 10^9$	3.8×10^9[f]
PNT	$(8.2 \pm 0.5) \times 10^9$	7.0×10^9[g]
MNT	$(8.6 \pm 0.5) \times 10^9$	–

The indicated error values correspond to one standard deviation. For comparative purposes available literature data are included.

[a] Lopez et al. (2000) (pH = 3.0).

[b] García Einschlag et al. (2002b).

[c] Onstein et al. (1999) (pH = 7.0).

[d] Pozdnyakov et al. (2000).

[e] Savel'eva et al. (1972) (pH = 9.0).

[f] Cercek and Ebert (1968) (pH = 7.0).

[g] Gonzalez et al. (1998).

3.2. Structure–reactivity analysis

The effect of substituents on reactivity can be quantitatively represented by the Hammett equation (Chapman and Shorter, 1972; March, 1991; Hansch and Leo, 1995):

$$\log(k_S) = \log(k_0) + \rho \cdot \sigma$$

where k_S and k_0 are the rate constants for the substituted and the unsubstituted compounds, σ is a measure of the electron withdrawing or donating abilities of the substituents and ρ is a measure of the sensitivity of the reaction to electronic effects. Hammett's relation is a useful tool for the analysis of the electronic effects on reactivity and some mechanistic conclusions can be drawn from the value of the reaction constant ρ (Chapman and Shorter, 1972; March, 1991).

In the present study we have used polysubstituted derivatives of nitrobenzene, therefore the correlation of the measured rate constants with the Hammett parameters are not straightforward. We have used the algebraic sum of the Hammett constants σ and σ^+ for *ortho* (Chapman and Shorter, 1972), *meta* and *para* (March, 1991; Hansch and Leo, 1995) positions, to estimate σ_{calc} and σ^+_{calc} in all free positions and also Cl substituted positions (i.e., ipso substitutions) for each substrate. A better Hammett correlation for σ_{calc} values in comparison with σ^+_{calc} values was observed. This may indicate little resonance contribution for the transition state (March, 1991; Hansch and Leo, 1995).

Table 3
Calculated Hammett parameter (σ_{calc}) and probable site of HO· radical attack for the nitroaromatic substrates investigated

Compound	σ_{calc}	Probable site of HO attack
CDNBA	2.43	2 and 6
CDNB	1.62	6
DNB	1.42	5
DNP	1.04	6
NBE	0.71	3 and 5
MNP	0.43	2 and 4
ONP	0.33	4 and 6
PNP	0.33	2 and 6
PNT	0.75	3 and 5
MNT	0.65	5

Since the reaction of HO· radicals with aromatic compounds is electrophilic in nature (Anbar et al., 1966), σ_{calc} is expected to be a minimum for the most probable site of attack. The minimum σ_{calc} values for the studied set of substrates are shown in Table 3.

Fig. 3 shows the Hammett correlation for the set of nitroaromatic compounds studied. Benzene (BEN), the unsubstituted compound with $\sigma = 0$, was also included for comparison (Ashton et al., 1995). The observed behavior suggests a common reaction mechanism for CDNBA, CDNB, DNB, DNP, NBE, MNP, ONP and PNP. However the observed degradation rates for PNT and MNT are much higher than those expected, therefore this substrates were not included in the correlation. The solid line represents the linear correlation whereas the dotted curves show the corresponding 99% confidence interval.

The slope ρ of the correlation is -0.60 ± 0.07. This value agrees with previously reported values for HO·

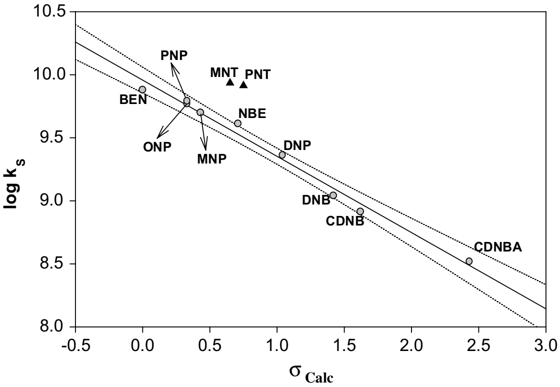

Fig. 3. Logarithmic plot of the rate constants (k_S) vs. the calculated Hammett parameter (σ_{calc}) for HO· radical reaction with substituted nitroaromatic compounds. For this set of substrates, $\log k_S = 9.96 - 0.60 \times \sigma_{\text{calc}}$ ($r = 0.993$).

radical addition to benzene rings (Neta and Dorfman, 1968). Negative values of ρ imply a reaction favored by high electron density at the reaction site, i.e., electrophilic attack. The small absolute value of ρ obtained is due to the high electron affinity and consequently the poor selectivity of $HO^{\cdot}$ radicals.

Two factors may be related to the high degradation rates observed for PNT and MNT. On one hand, UV photolysis of these compounds cannot be completely neglected because their quantum yields are higher than those for the other substrates (i.e., the rate constants k_S for PNT and MNT would be lower than the values presented in Table 2). On the second hand, hydroxyl radicals are known to abstract H atoms from aliphatic hydrocarbons (Ho, 1986; Stefan and Bolton, 1998), thus a reaction channel involving H abstraction from CH_3 groups might also contribute to the higher degradation rates observed for PNT and MNT (Dillert et al., 1995; Cencione et al., 1998).

4. Conclusions

Competitive experiments are useful to obtain kinetic information for AOP reaction models. The double logarithmic analysis allows a better estimation of the relative reactivity than the plots of ln[S] vs. *time* because it remains linear for larger degree of conversions and yields smaller errors. In order to avoid high experimental errors, the substrate and the compound used as reference should have comparable reactivities.

The rate constants obtained for the set of nitroaromatic substrates studied ranged from 0.33 to 8.6×10^9 $M^{-1}\,s^{-1}$ showing the effects of structure on reactivity. Assuming σ values to be additive, the effect of substituents can be quantitatively represented by a linear Hammett correlation. The small negative value of -0.60 obtained for ρ, agrees with both the high reactivity and the electrophilic nature of the $HO^{\cdot}$ radicals.

Acknowledgements

This work was supported in part by a project grant from the Agencia de Promoción Científica y Tecnológica de Argentina (ANPCyT grant no PICT 06-03531), the Consejo Nacional de Investigaciones Científicas y Tecnológicas (grant no PIP4354) and the University of La Plata (project no X-226). We also thank CINDECA for the HPLC facilities and Dr. Daniel O. Mártire for his valuable comments on the manuscript.

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