

NUCLEOPHILIC ACTIVITY OF PEROXYHYDROCARBONATE AND PEROXOCARBONATE IONS RELATIVE TO 4-NITROPHENYL DIETHYL PHOSPHONATE

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Peroxocarbonate ions HCO_4^- and CO_4^{2-} , which are formed in the $\text{H}_2\text{O}_2/\text{NH}_4\text{HCO}_3/\text{HO}^-$ system, react with 4-nitrophenyl diethyl phosphonate (I) through a nucleophilic mechanism with rate constants $k_{\text{HCO}_4^-} = 0.008$ and $k_{\text{CO}_4^{2-}} = 0.13 \text{ L/mol}\cdot\text{s}$. Comparison of these constants with the corresponding constants of other inorganic anions in their reaction with I in the framework of the Brönsted equation indicates that HCO_4^- and CO_4^{2-} are typical α -nucleophiles.

Key words: 4-nitrophenyl diethyl phosphonate, hydrogen peroxide, peroxyhydrocarbonate ion, peroxocarbonate ion, nucleophilicity.

In addressing the outstanding problem of eliminating ecologically toxic substances, recent attention has been given to the reactivity of systems containing hydrogen peroxide and its activators, primarily, ammonium and alkali metal hydrocarbonates [1-4]. Such systems, which fully meet the requirements of green chemistry, are universal and may be used for the decomposition of highly toxic organophosphorus compounds and sulfide derivatives by an oxidative-nucleophilic mechanism since the HO_2^- anion, which is a powerful α -nucleophile [5, 6], and the HCO_4^- ion [1-4], which is an effective oxidizing agent, are both generated in the aqueous $\text{H}_2\text{O}_2/\text{HCO}_3^-/\text{HO}^-$ system. On the other hand, there have been a few reports that HCO_4^- and CO_4^{2-} ions formed in the $\text{H}_2\text{O}_2/\text{HCO}_3^-$ system display nucleophilic properties [6-8]. In particular, in previous work [6], we noted that the HCO_4^- anion may act as a nucleophilic species in the decomposition of phosphates.

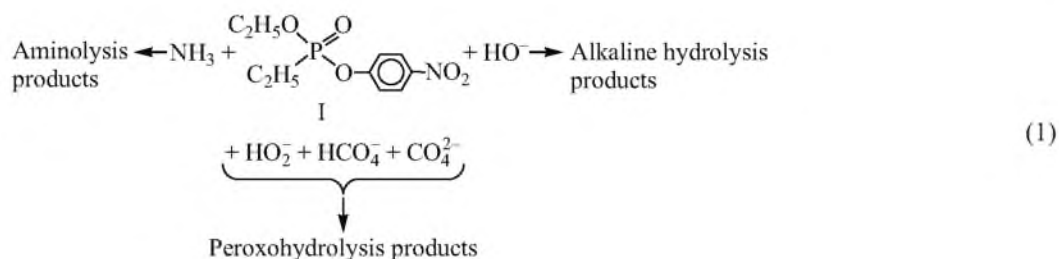
In the present work, we carried out a detailed kinetic study of the decomposition of 4-nitrophenyl diethyl phosphonate (I), which is a model for several pesticides and chemical warfare agents, by the $\text{H}_2\text{O}_2/\text{NH}_4\text{HCO}_3/\text{HO}^-$ system and evaluated the nucleophilic reactivity of the HCO_4^- and CO_4^{2-} ions in aqueous solution. These studies may provide information for optimizing processes for the decomposition of ecologically toxic substances.

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The decomposition of substrate I in the abovementioned system is complex and proceeds through at least five parallel channels:



Under pseudo-first-order conditions relative to the substrate, the equation for the observed rate constant k (s^{-1}) corresponds to this scheme

$$k = k_{\text{HO}^-} [\text{HO}^-] + k_{\text{HO}_2^-} [\text{HO}_2^-] + k_{\text{NH}_3} [\text{NH}_3] + k_{\text{HCO}_4^-} [\text{HCO}_4^-] + k_{\text{CO}_4^{2-}} [\text{CO}_4^{2-}], \quad (2)$$

where k_{HO^-} , $k_{\text{HO}_2^-}$, etc. are the second-order rate constants of the corresponding reaction pathways, $\text{L/mol}\cdot\text{s}$, and $[\text{HO}^-]$, $[\text{HO}_2^-]$, etc. are the equilibrium concentrations of the nucleophilic species. Equation (2) permits us to calculate $k_{\text{HCO}_4^-}$ and $k_{\text{CO}_4^{2-}}$ when the other rate constants and the equilibrium constants of all the species are known.

The values for k_{HO^-} , $k_{\text{HO}_2^-}$, and k_{NH_3} were found in independent experiments. The rate constant for the alkaline hydrolysis of I, $k_{\text{HO}^-} = 0.15 \text{ L/mol}\cdot\text{s}$ was determined in our previous work [5]. The rate constant for the perhydrolysis of I, $k_{\text{HO}_2^-}$, was calculated for solution ionic strength $\mu = 2.0 \text{ M}$ (KCl) using the following equation

$$k_1 = k_{\text{HO}_2^-} - \frac{1}{K_1} k_1 [\text{H}^+] \quad (3)$$

where $k_1 = (k - k_{\text{HO}^-} [\text{HO}^-]) / [\text{H}_2\text{O}_2]_0$, while K_1 is the acid dissociation constant of H_2O_2 [5]. Treatment of the data shown in Table 1 using Eq. (3) leads to the following equation

$$k_1 = (5.00 \pm 0.14) - (2.34 \pm 0.09) \cdot 10^{11} k_1 [\text{H}^+],$$

$$r = 0.987, s = 0.28, n = 17,$$

hence, $k_{\text{HO}_2^-} = (5.00 \pm 0.14) \text{ L/mol}\cdot\text{s}$, $K_1 = (4.27 \pm 0.16) \cdot 10^{-12} \text{ mol/L}$ ($k_{\text{HO}_2^-} = 7.3 \text{ L/mol}\cdot\text{s}$, $K_1 = 3.16 \cdot 10^{-12} \text{ mol/L}$ for $\mu = 1.0 \text{ M}$ (KCl) [5]).

The ammonolysis of I was studied in aqueous ammonia at $\mu = 2.0 \text{ M}$ (KCl). The equilibrium concentrations $[\text{NH}_3]$ were calculated using the acid dissociation constant of the NH_4^+ ion, $K = 5.66 \cdot 10^{-10}$ [10] and the experimental pH values (see the work of Bruce [9]). The following equation

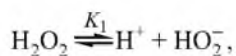
$$k - k_{\text{HO}^-} [\text{HO}^-] = k_{\text{NH}_3} [\text{NH}_3] \quad (4)$$

was used to calculate the ammonolysis rate constant $k_{\text{NH}_3} = (6.29 \pm 0.27) \cdot 10^{-5} \text{ L/mol}\cdot\text{s}$ ($r = 0.996$, $s = 2.5 \cdot 10^{-5}$, $n = 6$). We should note that our value for k_{NH_3} is very satisfactorily described by the Brønsted equation $\log k_{\text{amine}} = -7.4 + 0.35pK_a$, which correlates the reactivity of various types of amines relative to substrate I [11].

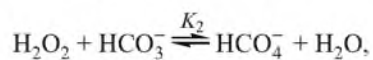
The equilibrium concentrations of HCO_4^- , CO_4^{2-} , and HO_2^- were calculated taking account of the following equilibria:

TABLE 1. Observed Rate Constants k for the Perhydrolysis of 4-Nitrophenyl Diethyl Phosphonate at 25 °C, $[\text{H}_2\text{O}_2]_0 = 0.00245 \text{ M}$, $\mu = 2.0 \text{ M (KCl)}$, KOH

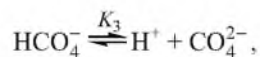
Expt. number	pH	$k \cdot 10^3, \text{ s}^{-1}$
1	10.04	0.623 ± 0.012
2	10.20	0.770 ± 0.010
3	10.40	1.15 ± 0.01
4	10.60	1.86 ± 0.01
5	10.75	2.47 ± 0.01
6	10.80	2.65 ± 0.02
7	11.00	3.59 ± 0.03
8	11.02	4.22 ± 0.02
9	11.25	5.67 ± 0.02
10	11.50	7.48 ± 0.02
11	11.50	7.37 ± 0.03
12	11.75	9.57 ± 0.05
13	12.00	14.7 ± 0.1
14	12.00	11.1 ± 0.1
15	12.25	14.6 ± 0.1
16	12.72	19.8 ± 0.3
17	12.76	19.9 ± 0.1



$$K_1 = 4.27 \cdot 10^{-12} \text{ mol/L} ,$$

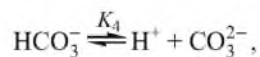


$$K_2 = 0.33 \text{ L/mol [1]} ,$$



$$K_3 = 3.98 \cdot 10^{-10} \text{ mol/L [1]} ,$$

$$K_3 = 2.51 \cdot 10^{-11} \text{ mol/L [2]} ,$$



$$K_4 = 4.68 \cdot 10^{-11} \text{ mol/L [12]} ,$$

and material balance equations:

$$[\text{HCO}_3^-]_0 = a = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{HCO}_4^-] + [\text{CO}_4^{2-}],$$

$$[\text{H}_2\text{O}_2]_0 = b = [\text{H}_2\text{O}_2] + [\text{HO}_2^-] + [\text{HCO}_4^-] + [\text{CO}_4^{2-}].$$

Solution of this system of six equations leads to the following expression for the equilibrium concentration $[\text{HCO}_3^-]$:

$$K_2 d f [\text{HCO}_3^-]^2 + [K_2 d (b - a) + c f] [\text{HCO}_3^-] - ac = 0 \quad (5)$$

where

$$c = 1 + \frac{K_1}{[\text{H}^+]}, d = 1 + \frac{K_3}{[\text{H}^+]}, f = 1 + \frac{K_4}{[\text{H}^]}.$$

The equilibrium concentrations of peroxo anions HCO_4^- and CO_4^{2-} as well as the starting concentrations of hydrogen peroxide and ammonium hydrocarbonate and the observed rate constants k are given in Table 2.

Let us represent Eq. (2) as

$$\Delta k = k_{\text{HCO}_4^-} [\text{HCO}_4^-] + k_{\text{CO}_4^{2-}} [\text{CO}_4^{2-}] \quad (6)$$

where

$$\Delta k = k - k_{\text{HO}^-} [\text{HO}^-] - k_{\text{HO}_2^-} [\text{HO}_2^-] - k_{\text{NH}_3} [\text{NH}_3]. \quad (7)$$

The system of conditional equations (6) must be solved in order to find the most probable values of $k_{\text{HCO}_4^-}$ and $k_{\text{CO}_4^{2-}}$. The corresponding calculation according to the data of Table 2 leads to the following correlation equation

$$\Delta k = -(0.29 \pm 0.15) \cdot 10^{-3} + (0.0077 \pm 0.0019) [\text{HCO}_4^-] + (0.1314 \pm 0.0049) [\text{CO}_4^{2-}], \quad (8)$$

$$R = 0.981, s_0 = 0.33 \cdot 10^{-3}, n = 32 \text{ (without points 26 and 27)}.$$

Further elimination of points does not significantly alter the coefficients for variables $[\text{HCO}_4^-]$ and $[\text{CO}_4^{2-}]$. Thus, we may assume that when $K_3 = 3.98 \cdot 10^{-10}$, the rate constants sought $k_{\text{HCO}_4^-} = (0.008 \pm 0.002)$ L/mol·s and $k_{\text{CO}_4^{2-}} = (0.13 \pm 0.01)$ L/mol·s. A statistically significant free term appears in Eq. (8) since the ionization rate constant of hydrogen peroxide K_1 and the rate constant $k_{\text{HO}_2^-}$ are determined in aqueous KCl while the reaction with I was carried out in aqueous NH_4Cl . However, as we have shown experimentally, this circumstance does not substantially affect the values of constants $k_{\text{HCO}_4^-}$ and $k_{\text{CO}_4^{2-}}$.

When $K_3 = 2.51 \cdot 10^{-11}$, a large scatter is observed for the values for Δk , $[\text{HCO}_4^-]$, and $[\text{CO}_4^{2-}]$, which prevents a statistically valid evaluation of constants $k_{\text{HCO}_4^-}$ and $k_{\text{CO}_4^{2-}}$. This situation arises, in all likelihood, as the result of an underestimated value of K_3 , which was determined in 20% aqueous ethanol [2]. The circumstance that the corresponding value of $\text{p}K_a = 10.6$ is overestimated is also indirectly indicated by our evaluation of this value using literature data (see below).

Thus, the reactivity of the CO_4^{2-} ion as a nucleophile toward I is 38 times lower than the corresponding value for the HO_2^- ion ($k_{\text{HO}_2^-} = 5.00$ L/mol·s). The rate constant for the nucleophilic reaction of the CO_4^{2-} ion with triphenyl thiophosphinate in aqueous ethanol $k_{\text{CO}_4^{2-}} = 210$ L/mol·s is ~2.3 times greater than $k_{\text{HO}_2^-}$ [8]. The reason for such a strong dependence of the rate of nucleophilic reactions of the CO_4^{2-} and HO_2^- ions on the nature of the substrate and/or the solvent has not yet been elucidated.

We compared the nucleophilic reactivity of peroxocarbonate ions HCO_4^- and CO_4^{2-} with the reactivity of other anionic inorganic nucleophiles in the framework of the Brønsted equation. This comparison is difficult since we do not know the true

TABLE 2. Peroxohydrolysis of 4-Nitrophenyl diethyl Phosphonate in the $\text{H}_2\text{O}_2/\text{NH}_4\text{HCO}_3/\text{HO}^-$ System in Water at 25 °C, $\mu = 2.0$ (NH_4HCO_3), $K_3 = 3.98 \cdot 10^{-10}$

Expt. number	pH	$[\text{H}_2\text{O}_2]_0$, mol/L	$[\text{NH}_4\text{HCO}_3]_0$, mol/L	$[\text{HCO}_4^-]10^2$, mol/L	$[\text{CO}_4^{2-}]10^2$, mol/L	$k \cdot 10^3$, s^{-1}	$\Delta k \cdot 10^3$, s^{-1}
1	7.67	0.242	2.0	9.26	0.172	1.22 ± 0.04	1.07
2	7.76	0.242	2.0	9.24	0.212	0.891 ± 0.024	0.706
3	7.78	0.242	2.0	9.24	0.222	0.973 ± 0.010	0.779
4	7.88	0.242	2.0	9.21	0.278	1.01 ± 0.01	0.766
5	7.90	0.242	2.0	9.21	0.291	1.10 ± 0.02	0.845
6	7.93	0.242	2.0	9.20	0.312	1.24 ± 0.02	0.964
7	8.09	0.242	2.0	9.13	0.447	1.45 ± 0.01	1.06
8	8.10	0.242	2.0	9.13	0.457	1.31 ± 0.02	0.908
9	8.15	0.242	2.0	9.10	0.512	1.60 ± 0.02	1.15
10	8.22	0.121	2.0	4.60	0.304	0.951 ± 0.009	0.683
11	8.50	0.178	2.0	6.53	0.822	2.66 ± 0.03	1.93
12	8.56	0.237	2.0	8.56	1.24	3.15 ± 0.04	2.04
13	8.60	0.227	2.0	8.16	1.29	3.81 ± 0.04	2.65
14	8.65	0.236	2.0	8.40	1.49	3.36 ± 0.04	2.02
15	8.73	0.483	2.0	16.40	3.51	8.12 ± 0.07	4.83
16	8.90	0.120	2.0	4.09	1.29	2.89 ± 0.03	1.71
17	9.00	0.116	2.0	3.82	1.52	2.66 ± 0.03	1.26
18	9.16	0.110	2.0	3.39	1.95	3.53 ± 0.02	1.69
19	9.19	0.0581	2.0	1.77	1.09	2.19 ± 0.01	1.11
20	9.50	0.219	2.0	5.30	6.67	16.4 ± 0.1	9.62
21	9.50	0.236	2.0	5.70	7.17	17.2 ± 0.1	9.89
22	9.56	0.0588	2.0	1.38	1.99	3.88 ± 0.01	1.71
23	9.72	0.0283	2.0	0.562	1.17	2.91 ± 0.07	1.46
24	9.75	0.0579	2.0	1.11	2.48	5.27 ± 0.06	2.43
25	9.90	0.0214	2.0	0.338	1.07	3.01 ± 0.09	1.48
26	9.50	0.220	1.8	5.05	6.35	13.5 ± 0.1	6.28
27	9.50	0.228	1.4	4.58	5.76	12.0 ± 0.1	3.54
28	9.75	0.057	1.6	0.993	2.22	5.63 ± 0.06	2.47
29	9.75	0.057	1.2	0.866	1.94	5.29 ± 0.03	1.64
30	9.75	0.057	1.0	0.784	1.75	6.34 ± 0.07	2.39
31	9.90	0.0229	1.8	0.349	1.10	2.97 ± 0.07	1.27
32	9.90	0.0225	1.6	0.327	1.04	3.24 ± 0.01	1.46
33	9.90	0.0222	1.4	0.306	0.967	3.21 ± 0.02	1.33
34	9.90	0.0227	1.2	0.292	0.922	3.26 ± 0.02	1.20

Note. The ionic strength in experiments 26-34 was maintained by an additional amount of KCl.

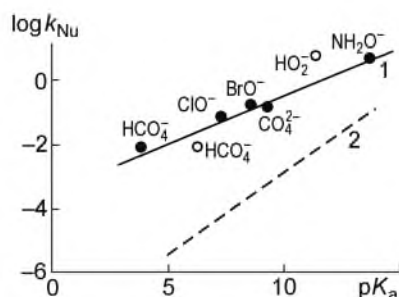


Fig. 1. Brønsted dependence for the reaction of inorganic α -nucleophiles (1) and arylate or alcoholate ions (2) with 4-nitrophenyl diethyl phosphonate. The k_{Nu} values (L/mol·s) for ClO^- , BrO^- , and NH_2O^- were taken from our previous work [5]. Curve 2 was constructed using the data of earlier work [13]. Curve 1 was constructed using the five closed circles.

basicities of the HCO_4^- and CO_4^{2-} ions. However, we may propose reasonable ranges for the actual values of the $\text{p}K_a$ values of these ions on the basis of literature data and several assumptions.

Since the kinetic parameters of the decomposition of peroxycarboxylic acid (to hydrogen peroxide and carbon dioxide) and of carbonic acid (to water and carbon dioxide) are similar to each other, Richardson et al. [1] proposed that the $\text{p}K_a$ values of the dissociation of these acids are approximately the same. Since the true $\text{p}K_a$ of carbonic acid is 3.9, while the apparent $\text{p}K_a$ is 6.35 [12], it is reasonable to assume that the $\text{p}K_a$ for HCO_4^- lies in the range 3.9-6.35.

We took $K_3 = 3.98 \cdot 10^{-10}$ for the acid dissociation equilibrium of the HCO_4^- ion using the $\text{p}K_a$ value for HCO_4^- ion (9.4) [1]. This latter value was obtained assuming that the $\text{p}K_a$ values for HCO_4^- and HSO_5^- are approximately the same. An approximate evaluation of $\text{p}K_a$ for HCO_4^- as an acid may also be obtained from the pH dependence of the rate of oxidation of several organic sulfides in the $\text{H}_2\text{O}_2/\text{NH}_4\text{HCO}_3/\text{HO}^-$ system: 2-hydroxyethyl phenyl sulfide [2], diethyl sulfide [3], and methyl phenyl sulfide [4]. In all three reactions in the pH range from about 7 to 9, the rate is virtually independent of pH ($\text{p}K_a > \text{pH}$, the HCO_4^- anions predominantly participate in the oxidation). The rate decreases with an increase in pH above 9 (the oxidation is carried out concurrently by the HCO_4^- and CO_4^{2-} ions). At pH 10-11, the rate reaches a plateau ($\text{p}K_a < \text{pH}$, the CO_4^{2-} ions participate predominantly in the oxidation). The point corresponding to $\text{p}K_a = \text{pH}$ is within the range of the pH values, in which the rate decreases. The midpoint of this range may be taken as the approximate $\text{p}K_a$ of the HCO_4^- ion. A graphic evaluation gives the following $\text{p}K_a$ values: ~ 10 [2], ~ 9.8 [3], ~ 9.0 [4]. Thus, we may assume that the $\text{p}K_a$ for HCO_4^- as an acid (or the $\text{p}K_a$ for CO_4^{2-} as a base) is in the range 9.0-10.0.

A comparison of the values obtained for $k_{\text{HCO}_4^-}$ and $k_{\text{CO}_4^{2-}}$ with the rate constants of the reaction of I with other anionic inorganic nucleophiles is shown in Fig. 1 as a Brønsted dependence. In this case, it is more logical to use the true value $\text{p}K_a = 3.9$ (closed circles) for HCO_4^- . The open circle corresponds to the apparent $\text{p}K_a = 6.35$. We took $\text{p}K_a = 9.4$ for CO_4^{2-} . The points for HCO_4^- and CO_4^{2-} lie significantly higher than curve 2 ($\Delta \log k_{\text{HCO}_4^-} = 3.9$, $\Delta \log k_{\text{CO}_4^{2-}} = 2.4$, closed circles), which corresponds to the reaction of I with arylate or alcoholate ions (standard reaction series) [13] and forms a single Brønsted dependence with well-known α -nucleophiles ClO^- , BrO^- , and NH_2O^- (line 1) (see our previous work [5]):*

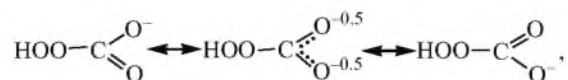
*When the apparent $\text{p}K_a = 6.35$ (open circle) is used for HCO_4^- , the statistical criteria for correlation (9) are much less satisfactory.

$$\log k_{\text{Nu}} = -(3.21 \pm 0.18) + (0.27 \pm 0.02)\text{p}K_{\text{a}}, \quad (9)$$

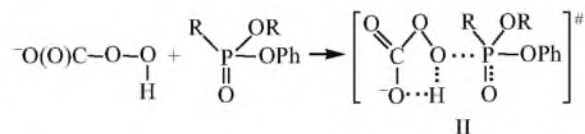
$$r = 0.992, \quad s_0 = 0.14, \quad n = 5.$$

This finding permits us to regard the HCO_4^- and CO_4^{2-} ions as typical α -nucleophiles, which display supernucleophilic reactivity relative to substrate I. This conclusion is independent of our choice of $\text{p}K_{\text{a}}$ values within the ranges given above.

We should especially examine the reasons for the anomalously high reactivity of the peroxyhydrocarbonate ion, which has hydrocarbonate structure $\text{HOOC}(\text{O})\text{O}^-$ [14]:



rather than $^-\text{OOC}(\text{O})\text{OH}$ and this may serve as the formal basis for our conclusion of similar reactivity of the HCO_4^- and HCO_3^- ions in nucleophilic reactions. It would appear that the HCO_3^- anion is an extremely weak nucleophile. The reactivity of this anion should be less than the reactivity of the more basic CO_3^{2-} anion. On the other hand, the CO_3^{2-} anion is a weak nucleophile. For example, the CO_3^{2-} anion in its reaction with 4-nitrophenyl acetate shows a significant negative deviation from the Brønsted correlation for “normal” oxygen and nitrogen reagents [15]. In all likelihood, the reason for the “nonstandard” kinetic behavior of the HCO_4^- anion is related to the possibility of intramolecular hydrogen bonding in transition state II, which leads to its stabilization:



The formation of intramolecular hydrogen bonds and proton transfer occur here in an energetically-favorable five-membered ring and the peroxide oxygen atom acts as the reaction site as in oxidation reactions [2]. Similar behavior is seen in the case of the neutral form of hydroxylamine, which is an oxygen nucleophilic reagent (rather than a nitrogen reagent) and is regarded as a typical α -nucleophile [5].

We should note that the HCO_4^- anion has the lowest basicity ($\text{p}K_{\text{a}} = 3.9$) of all the presently known inorganic α -nucleophiles.

EXPERIMENTAL

A sample of 4-nitrophenyl diethyl phosphonate was obtained and purified as in our previous work [5]. In the present work, we used analytical-grade 25% aqueous ammonia, chemically-pure-grade ammonium bicarbonate, analytical-grade potassium hydroxide, analytical-grade potassium chloride, and doubly distilled water. The concentration of the major compound in the hydrogen peroxide solution was determined by permanganate titration [16].

We added $\sim 1 \cdot 10^{-4}$ mol/L trilon B to stabilize the hydrogen peroxide in the working solution. For each pH value, the $\text{H}_2\text{O}_2\text{-NH}_4\text{HCO}_3$ solution was maintained for at least 20 min in order to establish equilibrium. The required pH values were obtained by adding small amounts of aqueous potassium hydroxide or aqueous ammonia. An OR-211/1 pH-meter was used to measure the pH. The reactions were studied in water at 25 °C with ionic strength $\mu = 2.0$ maintained with NH_4HCO_3 and KCl. The reaction course was monitored by UV spectroscopy relative to the change in adsorption of the 4-nitrophenolate ion over time ($\lambda = 410$ nm) on an SF-26 spectrometer. The initial substrate concentration ($\sim 5 \cdot 10^{-5}$ mol/L) was much lower than the initial concentration of H_2O_2 . The method for calculating the pseudo-first-order rate constants was examined in our previous work [5]. We should note that, under our experimental conditions, the concentration of liberated 4-nitrophenolate ion at the end

of the reaction corresponded to the initial concentration of the substrate, which indicates that there was no oxidation of the substrate during the reaction.

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