UDC 547:541.127/.8

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PEROXYHYDROCARBONATE AND PEROXOCARBONATE IONS AS TYPICAL α-NUCLEOPHILES IN PHOSPHONYL TRANSFER[*]

In a search for novel, high-reactivity, α-nucleophiles we examined the kinetics of decomposition of 4-nitrophenyldiethyl phosphonate (NPDEPN) by $H_2O_2/NH_4HCO_3/HO^-$ at pH 7.7—10.4. This system generates HCO_4^- and CO_4^{2-}, and their equilibrium concentrations were calculated with the corresponding equilibrium constants, allowing estimation of second-order rate constants for nucleophilic reactions with NPDEPN, $k_{HCO_4^-} = 0.006$ and $k_{CO_4^{2-}} = 0.18$ $M^{-1} \cdot s^{-1}$ (25 $^{\circ}$C, $\mu = 2.0$ M). As shown by comparisons of Bronsted relationships of the rate constants with those for other anionic nucleophiles in dephosphonylation of NPDEPN, HCO_4^- and CO_4^{2-} ions are typical α-nucleophiles. These findings can be significant in selection of optimum conditions for decomposition of various ecotoxicants.

INTRODUCTION. Typical inorganic α-nucleophiles such as hypochlorite, hypobromite and hydroperoxide ions, neutral and anionic forms of hydroxylamine, exhibit abnormally high reactivity (α-effect), as expected from Bronsted relationships for "normal" oxygen nucleophiles (aryloxide, alkoxide ions, HO^- and H_2O) [1–4]. Possible applications of these inorganic nucleophiles is their use in systems for efficient destruction of ecotoxicants — pesticides, chemical warfare agents, etc. [5–7]. Of special interest are mixtures of hydrogen peroxide with activators [6–12], e.g., alkaline metal and ammonium hydrocarbonates because aqueous $H_2O_2/HCO_3^-/HO^-$ mixtures contain the strong α-nucleophile, HO_2^-, and an efficient oxidant, HCO_4^- [4, 6–12] allowing design of versatile oxidizing-nucleophilic systems for "green" decomposition of highly toxic phosphorus esters through nucleophilic attack by HO_2^- and other peroxyions, and of sulfide derivatives, e.g., Mustard Gas, by oxidation with HCO_4^- [5, 6]. There is evidence that both HCO_4^- and CO_4^{2-}, which are formed in this system, react as nucleophiles [13–16]. Until recently it was uncertain whether these ions are normal oxygen or α-nucleophiles. Structurally, CO_4^{2-} meets the requirements of α-nucleophiles: i) the nucleophilic center (oxygen) is anionic and is in the second period of the Periodic Table; ii) there are no adjacent substituents sterically hindering attack on the electrophilic center in the substrate; iii) electronegative oxygen with unshared electron pairs is α- to the reaction center of the reagent, which destabilizes the ground state and stabilizes the transition state of the reaction [17, 18]. It is difficult to predict, a priori, the kinetic behavior of HCO_4^- although it should be considerably less nucleophilic than the dianion.

In this work we studied the decomposition kinetics of 4-nitrophenyldiethyl phosphonate (NPDEPN) as a low-toxicity model of some pesticides and chemical agents with $H_2O_2/NH_4HCO_3/HO^-$, and estimated nucleophilicities of aqueous HCO_4^- and CO_4^{2-} (c.f. [16]). Such research can be useful in selection of optimum conditions for decomposition of ecotoxicants.

As a source of HCO_3^- we used ammonium hydrogen carbonate because this compound is readily soluble in water, reasonably stable in the presence of hydrogen peroxide, and leaves no inorganic residue after reaction. However, we had to allow for reaction of NH_3 in these conditions.

EXPERIMENTAL PART. Synthesis and purification of NPDEPN are described [4]. The analytically pure reagents were 25 % aqueous ammonia, ammonium hydrogen carbonate and chloride, potassium hydroxide and chloride, and bidistilled water. Concentrations of hydrogen peroxide solutions were determined by titration with permanganate ion [19].

Hydrogen peroxide in the working solutions was stabilized by Trilon B (10^{-4} M). Solutions of H_2O_2—NH_4HCO_3 were equilibrated for *ca.* 20 min at each pH. The pH was controlled by KOH or by addition of a certain volume of NH_4OH of the known concentration, pH was measured on a Metrohm 744. Kinetics were in water at 25 $^{\circ}$C, ionic strength (μ) 2.0, main-

tained with NH_4HCO_3, NH_4Cl, or, where necessary, KCl. Reactions were monitored by following the increasing absorbance of 4-nitrophenoxide ion at λ 410 nm on a Genesis 10 UV (Thermo Electron) spectrophotometer. Hydrogen peroxide was in large excess over the substrate ($\approx 5 \cdot 10^{-5}$ M). Decomposition of H_2O_2 during the time of reaction did not cause problems, but it increased slightly if KOH was used to control pH. Calculation of the first-order rate constants was as described [4]. After complete reaction the concentration of 4-nitrophenoxide ion was that of the initial substrate. The reported first-order rate constants are averages of up to 12 results agreeing within 3 %.

RESULTS AND DISCUSSION. Decomposition of NPDEPN in the reaction conditions involves five parallel pathways (scheme) and the very slow reaction with H_2O, which is not kinetically important:
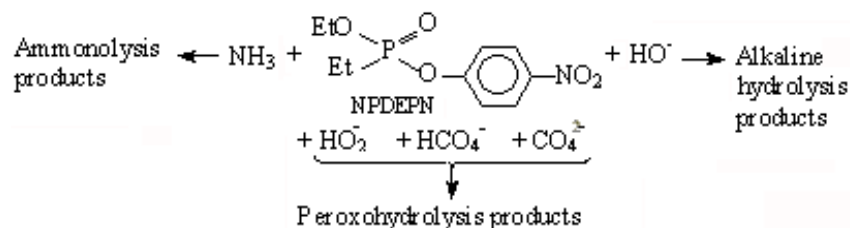
The observed first-order rate constant with respect to substrate, k, s^{-1} is given by equation:

$$k = k_{HO^-}[HO^-] + k_{HO_2^-}[HO_2^-] + k_{NH_3}[NH_3] + {} + k_{HCO_4^-}[HCO_4^-] + k_{CO_4^{2-}}[CO_4^{2-}], \quad (1)$$

where k_{HO^-}, $k_{HO_2^-}$, k_{NH_3}, $k_{HCO_4^-}$, $k_{CO_4^{2-}}$ are second-order rate constants ($M^{-1} \cdot s^{-1}$) of the corresponding reactions, and quantities in square brackets are equilibrium concentrations of the nucleophiles. Equation (1) allows calculation of $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$ after allowance for contributions of reactions of the other nucleophiles, which are known from independent experiments, and the corresponding concentrations can be estimated with known equilibrium constants. The overall reactions were followed over the pH range 7.67—10.4.

Values of $k_{HO_2^-}$ and k_{NH_3} were measured independently, and $k_{HO^-} = 0.15$ $M^{-1} \cdot s^{-1}$ had been determined earlier [4].

Ammonolysis of NPDEPN was studied in aqueous ammonia at $\mu = 2.0$ M (NH_4HCO_3 or KCl), see table 1. Equilibrium concentrations [NH_3] were

T a b l e 1

Ammonolysis of 4-nitrophenyldiethyl phosphonate (water, $t = 25$ °C, $\mu = 2.0$ M (NH_4HCO_3 or KCl)

pH	$(k - k_{HO^-}[HO^-])$ $\cdot 10^5$, s^{-1}	$[NH_3]_0$	$[NH_4HCO_3]_0$	$[NH_3]$
			M	
9.60	16.6	2.66	2	3.23
10.22	39.1	5.33	2	6.63
10.56	61.9	7.99	2	9.53
10.79[a]	0.340	0.0266	—	0.0259
11.00[a]	0.600	0.0533	—	0.0524
11.49[a]	4.35	0.533	—	0.530

[a] Ionic strength was controlled by KCl.

calculated [20] with the acid dissociation constant [21] of NH_4^+ $K_a = 5.66 \cdot 10^{-10}$ and the experimental pH and kinetics fitted equation (2):

$$k - k_{HO^-}[HO^-] = k_{NH_3}[NH_3]. \quad (2)$$

The rate constant of ammonolysis is $k_{NH_3} = (6.29 \pm 0.27) \cdot 10^{-5}$ $M^{-1} \cdot s^{-1}$ ($r = 0.996$, $s_o = 2.5 \cdot 10^{-5}$, $n = 6$) and fits the Bronsted equation ($\log k_{amine} = -7.4 + 0.35 p K_a$) for amine reactions with NPDEPN [22].

The second-order rate constant $k_{HO_2^-}$ and the acid dissociation constant of hydrogen peroxide, K_1, were measured in aqueous NH_4Cl ($\mu = 2.0$ M) and fitted to eqn. (3) as in ref. [4], with allowance for reactions with OH^- and NH_3:

$$k_1 = k_{HO_2^-} - \frac{1}{K_1} k_1 [H^+], \quad (3)$$

where k_1, $M^{-1} \cdot s^{-1}$ is the product of rate constant $k_{HO_2^-}$ and the fraction of HO_2^-:

$$k_1 = k_{HO_2^-} \frac{[HO_2^-]}{[H_2O_2]_o} = {} = \frac{k - k_{HO^-}[HO^-] - k_{NH_3}[NH_3]}{[H_2O_2]_o}. \quad (4)$$

The results are in table 2 and with equation (3) fit equation (5):

$$k_1 = (3.51 \pm 0.17) - (3.42 \pm 0.25) \cdot 10^{11} k_1 [H^+], \quad (5)$$
$$r = 0.982, \quad s_o = 0.21, \quad n = 9,$$
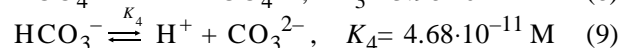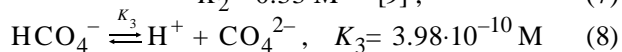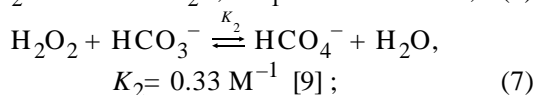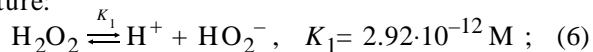
T a b l e 2

Observed rate constants k of decomposition of 4-nitrophe-nyldiethyl phosphonate in $H_2O_2/NH_4Cl/HO^-$ ($[H_2O_2]_0$ 0.00246 M, $\mu = 2.0$ M (NH_4Cl), KOH, 25 °C)

pH	$[NH_3]$, M	$k \cdot 10^3$, s^{-1}
10.25	1.82	0.622 ± 0.010
10.50	1.89	0.882 ± 0.010
10.75	1.94	1.28 ± 0.02
11.00	1.97	2.30 ± 0.01
11.25	1.98	3.30 ± 0.02
11.50	1.99	4.86 ± 0.02
11.75	1.99	6.68 ± 0.07
12.00	2.00	8.13 ± 0.05
12.25	2.00	9.82 ± 0.07

and, $k_{HO_2^-} = (3.51 \pm 0.17)$ $M^{-1} \cdot s^{-1}$, $K_1 = (2.92 \pm 0.21) \cdot 10^{-12}$ M. These values are in reasonable agreement with those in different conditions viz. $k_{HO_2^-} = 7.3$ $M^{-1}s^{-1}$, $K_1 = 3.16 \cdot 10^{-12}$ M, $\mu = 1.0$ M (KCl) [4] and $k_{HO_2^-} = 5.00$ $M^{-1} \cdot s^{-1}$, $K_1 = 4.27 \cdot 10^{-12}$ M, $\mu = 2.0$ M (KCl) [16].

The constants $k_{HO_2^-}$ and K_1 in 2 M NH_4Cl are lower than those in 2 M KCl, probably due to specific interactions of H_2O_2 and HO_2^- with NH_3, and equilibrium formation of hydrogen bond complexes by analogy with interaction of hydroperoxides with tertiary amines [23]. A large excess of ammonia ($[NH_3] / [H_2O_2]_0 \approx 800$, table 2) favors formation of such complexes. As shown later, this formation does not significantly affect values of $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$.

The calculations were made with equilibria equations (6)—(9), largely with data from the cited literature:

$$H_2O_2 \overset{K_1}{\rightleftharpoons} H^+ + HO_2^-, \quad K_1 = 2.92 \cdot 10^{-12} \text{ M} ; \quad (6)$$

$$H_2O_2 + HCO_3^- \overset{K_2}{\rightleftharpoons} HCO_4^- + H_2O,$$
$$K_2 = 0.33 \text{ M}^{-1} \text{ [9]} ; \quad (7)$$

$$HCO_4^- \overset{K_3}{\rightleftharpoons} H^+ + CO_4^{2-}, \quad K_3 = 3.98 \cdot 10^{-10} \text{ M} \quad (8)$$

$$HCO_3^- \overset{K_4}{\rightleftharpoons} H^+ + CO_3^{2-}, \quad K_4 = 4.68 \cdot 10^{-11} \text{ M} \quad (9)$$

and material balance:

$$[HCO^{3-}]_0 = [HCO_3^-] + [CO_3^{2-}] +$$
$$+ [HC_4^-] + [CO_3^{2-}], \quad (10)$$
$$[H_2O_2]_0 = [H_2O_2] + [HO_2^-] +$$

$$+ [HCO_4^-] + [CO_4^{2-}] . \quad (11)$$

Equilibrium concentrations of peroxoanions HO_2^-, HCO_4^- and CO_4^{2-} together with related rate constants, k, equilibrium concentrations of ammonia and initial concentrations of hydrogen peroxide are in table 3.

The second-order rate constants for contributions of the peroxocarbonate reactions are given by equation (12), which is derived from equation (1):

$$\Delta k = k_{HCO_4^-}[HCO_4^-] + k_{CO_4^{2-}}[CO_4^{2-}], \quad (12)$$

where $\Delta k = k - k_{HO^-}[HO^-] - k_{HO_2^-}[HO_2^-] -$
$$- k_{NH_3}[NH_3], \quad (13)$$

and table 3 includes values of Δk, equation (13).

It is significant that the overall contribution from the peroxycarbonate ion reactions to the observed rate constant [i.e. $\Delta k/k$ ratio, see eqns. (12) and (1)] is generally 70—90 %, indicating that uncertainties in contributions of the other reactions, eqn. (1), are not very important. Comparison of Δk, for reactions of $[HCO_4^-]$, and $[CO_4^{2-}]$ at similar initial $[H_2O_2]_0$ shows (table 3) that an increase in pH, and therefore in $[CO_4^{2-}]$, increases Δk, while $[HCO_4^-]$ decreases it (runs 2—9, 10 and 16, and 12, 14, and 22). Therefore the main contribution to Δk [equation (12)] is, as expected, from $k_{CO_4^{2-}}[CO_4^{2-}]$. Linear correlation, Δk versus $[CO_4^{2-}]$ neglecting the contribution of reaction with HCO_4^- gives:

$$\Delta k = (0.13 \pm 0.14) \cdot 10^{-3} + (0.181 \pm 0.007)[CO_4^{2-}], \quad (14)$$
$$r = 0.983, \quad s_0 = 6 \cdot 10^{-4}, \quad n = 29,$$

and $k_{CO_4^{2-}} = 0.18$ $M^{-1} \cdot s^{-1}$.

Rate constant $k_{HCO_4^-}$ can be estimated by the two-parameter correlation equation (12), of Δk versus $[HCO_4^-]$ and $[CO_4^{2-}]$ giving equation:

$$\Delta k = -(0.00024 \pm 0.00020) + (0.0063 \pm 0.0025) \cdot$$
$$\cdot [HCO_4^-] + (0.183 \pm 0.006)[CO_4^{2-}], \quad (15)$$
$$R = 0.986, \quad s_0 = 5 \cdot 10^{-4}, \quad n = 29.$$

As expected, the value of rate constant, $k_{CO_4^{2-}}$, from this equation is essentially that from eqn. (14). Elimination of the most strongly deviating points does not significantly affect constants for reactions involving $[HCO_4^-]$ and $[CO_4^{2-}]$.

Thus, estimated rate constants are $k_{HCO_4^-} = (0.006 \pm 0.002)$ $M^{-1} \cdot s^{-1}$ and $k_{CO_4^{2-}} = (0.18 \pm 0.01)$

T a b l e 3

Peroxohydrolysis of 4-nitrophenyldiethyl phosphonate in H_2O_2/ NH_4HCO_3/HO^- (water, $t=25\ ^{\circ}C$, $\mu =2.0$ M, $[NH_4HCO_3]_0 = 2.00$ M)

pH	$[H_2O_2]_0$, M	$k\cdot10^3$, s^{-1}	$[NH_3]$	$[HO_2^-]$ $\cdot10^4$	$\Delta k\cdot10^3$, s^{-1}	$[HCO_4^-]$ $\cdot10^2$	$[CO_4^{2-}]$ $\cdot10^3$
				M			M
7.67	0.242	1.22	0.0516	0.202	1.15	9.26	1.72
7.76	0.242	0.891	0.0656	0.248	0.800	9.24	2.12
7.78	0.242	0.973	0.0695	0.259	0.878	9.24	2.22
7.88	0.242	1.01	0.0878	0.326	0.890	9.21	2.78
7.90	0.242	1.10	0.0929	0.341	0.974	9.21	2.91
7.93	0.242	1.24	0.102	0.365	1.11	9.20	3.12
8.09	0.242	1.45	0.151	0.525	1.26	9.13	4.47
8.10	0.242	1.31	0.151	0.537	1.11	9.13	4.57
8.15	0.242	1.60	0.176	0.601	1.38	9.10	5.12
8.22	0.121	0.951	0.206	0.349	0.815	4.60	3.04
8.50	0.178	2.66	0.488	0.963	2.29	6.54	8.22
8.56	0.237	3.15	0.477	1.47	2.60	8.57	12.4
8.60	0.227	3.81	0.515	1.54	3.24	8.16	12.9
8.65	0.236	3.36	0.565	1.78	2.70	8.41	14.9
8.73	0.483	8.12	0.715	4.44	6.52	16.4	35.1
8.90	0.120	2.89	1.03	1.53	2.29	4.09	12.9
8.97	0.125	2.38	1.15	1.85	1.66	4.16	15.5
9.00	0.116	2.66	1.12	1.82	1.95	3.83	15.2
9.16	0.110	3.53	1.62	1.88	2.59	3.39	19.5
9.19	0.0581	2.19	1.81	1.32	1.61	1.78	10.9
9.50	0.219	16.4	2.57	9.07	13.1	5.31	66.8
9.50	0.236	17.2	2.57	9.80	13.6	5.71	71.8
9.56	0.0588	3.83	3.14	2.63	2.70	1.38	19.9
0.72	0.0283	2.91	3.89	1.64	2.08	0.564	11.8
9.75	0.0579	5.27	3.90	3.55	3.77	1.11	24.8
9.90	0.0214	3.01	5.00	1.65	2.11	0.340	10.7
10.08	0.0155	2.86	6.39	1.57	1.89	0.188	8.99
10.40	0.00933	2.74	9.34	1.56	1.57	0.180	6.41
10.40	0.00860	2.23	9.34	1.43	1.10	0.0591	5.91

$M^{-1}\cdot s^{-1}$. There apparently is a contribution of a reaction with HCO_4^- but it is not large and the value of $k_{HCO_4^-}$ is uncertain. Slightly different values were given earlier [16], because here we use a revised value of $k_{HO_2^-}$ and K_1 was determined with ionic strength maintained with 2 M NH_4Cl rather than with KCl. The observed rate constants k agree with k_{calc} calculated from equation (1) with values of $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$ (fig. 1):

$$k = -(0.23 \pm 0.13)\cdot10^{-3} +$$
$$+ (1.01 \pm 0.02)k_{calc}, \qquad (16)$$
$$r=0.992, \qquad s_o=5\cdot10^{-4}, \quad n=29.$$

The plot in fig. 1 has unit slope and a near zero intercept, as expected from equation (16), and is based on the data in table 3.

The value of $K_3 =3.98\cdot10^{-10}$ is reasonable in terms of similarities in pK_a of HCO_4^- and HSO_5^- (that of HSO_5^- is 9.4 [8]). An approximate pK_a of HCO_4^- can also be estimated from pH-rate profiles for oxidations of organic sulfides, 2-hydroxyethylphenyl [10], diethyl [11] and methylphenyl sulfide [12] in H_2O_2/ NH_4HCO_3/HO^-. The rates of oxidation by HCO_4^- are almost pH-independent in the range ~7—9, consistent with $pK_a > pH$, followed by rate decreases with increasing pH, with oxidations by HCO_4^- and CO_4^{2-}, tending to a constant rate at pH 10—11 with $pK_a < pH$ and the weaker oxidant, CO_4^{2-}, being the dominant species. The point for $pK_a = pH$ is in the pH-range of decreasing rates. The mid-point of the pH-rate profile should approximate the pK_a of HCO_4^- giving values of $pK_a \sim 10$ [10], ~9.8 [11], ~9.0 [12] and therefore pK_a of HCO_4^- should be in the range 9.0 —10.0. These results are consistent with $K_3 =3.98\cdot10^{-10}$.

Thus, the reactivity of CO_4^{2-} ion (as a nucleophile) toward NPDEPN is ca. 20 fold lower than that of HO_2^- ($k_{HO_2^-} =3.51$ $M^{-1}\cdot s^{-1}$). However, the estimated rate constant of the reaction of CO_4^{2-} and triphenyl phosphinate in aqueous alcohol, $k_{CO_4^{2-}} =210$ $M^{-1}\cdot s^{-1}$ is ≈ 2.3 fold higher than $k_{HO_2^-}$ [15] indicating that effects of substrate structure and solvent composition on nucleophilicities of CO_4^{2-} and HO_2^- have to be considered.

It is useful to examine Bronsted relationships in comparing nucleophilicities of HCO_4^- and CO_4^{2-} with those of "normal" anionic oxygen nucleophiles [3] and anionic inorganic α-nucleophiles [4], provided that appropriate basicities can be established.

Kinetic parameters for decompositions of peroxycarbonic acid (to hydrogen peroxide and carbon dioxide) and carbonic acid (to water and carbon dioxide) are similar, and Richardson et al. [8] suggested that this is also the situation for the first-stage
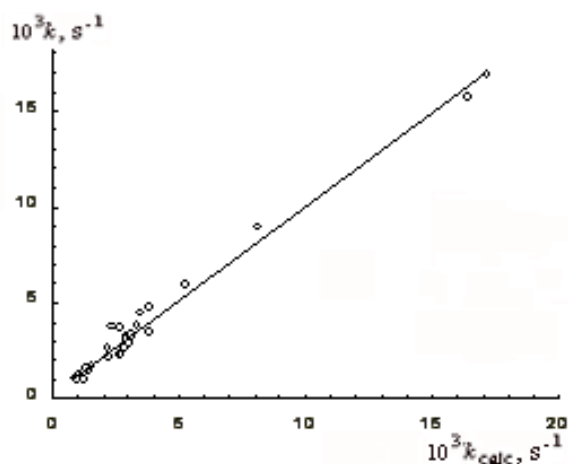
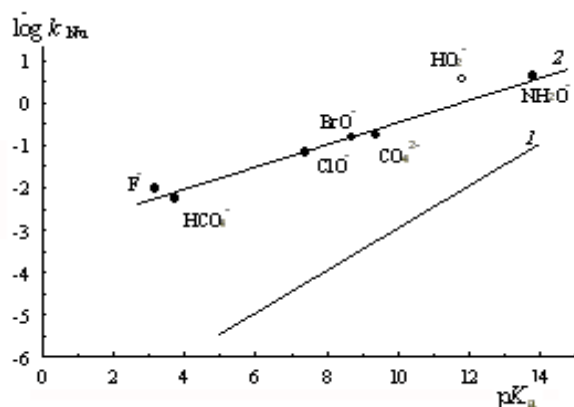Fig. 1. Observed rate constants k versus calculated k_{calc}.

Fig. 2. Bronsted plots for reactions of aryloxide/alkoxide ions (*1*) and inorganic α-nucleophiles (*2*) with 4-nitrophenyldiethyl phosphonate. Values of k_{Nu}, $M^{-1} \cdot s^{-1}$ for ClO^-, BrO^-, NH_2O^- and F^- are from ref. [4]. Statistical correction for pK_a of HCO_4^- and CO_4^{2-} is 0.30. Line *1* is from data in ref. [3]; line *2* is from the solid points, see text.

acid dissociation constants, pK_a, which would give, as a base, $pK_a (HCO_4^-) = 3.45$, i.e. close to the true pK_a of HCO_3^- rather than the apparent value in water for HCO_3^- 6.35 [24].

Bronsted plots for dephosphonylation of NPDEPN with our values of $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$ are shown in fig. 2, line *2*, with data for reactions with other anionic inorganic nucleophiles. The reactions with HCO_4^- and CO_4^{2-} are much faster those of NPDEPN with aryloxide/alkoxide ions (line *1*), a standard reaction series [3]. Rate differences correspond to

$\Delta log k_{HCO_4^-} = 3.8$ and $\Delta log k_{CO_4^{2-}} = 2.5$ with and respectively, with the behaviour typical of α-nucleophiles with supernucleophilic reactivity toward NPDEPN.

Reactivities towards NPDEPN of the anionic α-nucleophiles, including ClO^-, BrO^- and NH_2O^-, and F^- *, which is a strong nucleophile in dephosphorylations [4], are described by the Bronsted relationship, where k_{Nu} is the appropriate second-order rate constant:

$$log k_{Nu} = -(2.9 \pm 0.2) + (0.25 \pm 0.02)pK_a . \quad (17)$$

Introduction of rate constants for HCO_4^- and CO_4^{2-} into the equation also gives a single Bronsted relationship (line *2* in fig. 2):

$$log k_{Nu} = -(3.06 \pm 0.14) + (0.26 \pm 0.02)pK_a , \quad (18)$$
$$r = 0.992, \quad s_0 = 0.14, \quad n = 6.$$

The fact that $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$ fit on the correlation line, with little change in the coefficients, indicates that possible specific solvation of HCO_4^- and CO_4^{2-} ions by NH_4^+ and NH_3 or its complexation with H_2O_2 have little effect on the reactivity of the peroxocarbonate ions.

The simple relationship equation (18) indicates that common features control the kinetic behavior of these inorganic nucleophiles towards NPDEPN, with rates of phosphonyl transfer being sensitive to nucleophile basicities [4]. The slope of the plot of $log k_{Nu}$ against pK_a is consistently lower for α- than for simple nucleophiles as in fig. 2, lines *2* and *1* (the slopes are 0.26 and 0.50 [3] respectively).

The point for HO_2^- falls above line *2*. This apparent high reactivity of HO_2^- may be due to transition state stabilization by hydrogen bonding with the equatorial oxygen atom [4] (I). The corresponding hydrogen bonding by NH_2 in NH_2O^- would be less important and this nucleophile fits on line *2* (fig. 2).
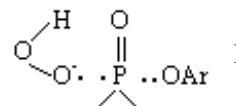

The reactivity of HCO_4^- and the fit to the Bronsted relationship, are interesting because X-ray crystallography indicates that the resonance stabilized structure II, is $HOOC(O)O^-$, in the solid and probably also in solution [25], rather than $^-OOC(O)OH$. If this structure solely governed reactivity the nucleo-

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* While F^- ion is not an α-nucleophile, in nucleophilic substitutions at phosphoryl and phosphonyl centers it has reactivities similar to that of anionic inorganic α-nucleophile of the same basicity [4].

$$II$$
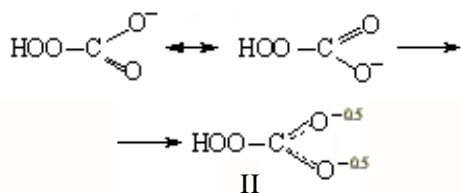
philicity of HCO_4^- should be similar to that of weakly nucleophilic HCO_3^- and less than of CO_3^{2-}, also a weak nucleophile, e.g., in the reaction of CO_3^{2-} with 4-nitrophenyl acetate there is a significant negative deviation from the Bronsted plot for other "normal" oxygen and nitrogen nucleophiles [1]. As suggested for the abnormally high reactivity of the neutral hydroxylamine [4, 26, 27] and amidoxime [28, 29] derivatives and hydroxamate ions [29—31], this "non-conventional" kinetic behavior of HCO_4^- may be due to stabilizing intramolecular hydrogen bonding in the transition state III:
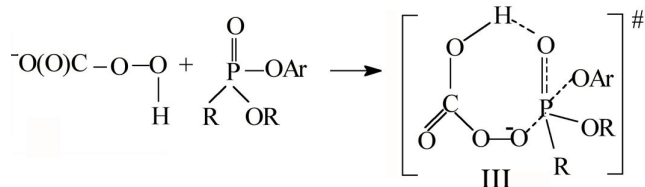
Hydrogen bonding and proton transfer are shown in an energetically favorable seven-membered ring and, as with oxidation [8, 9], peroxy oxygen is at the reaction center. Formation of the transition state, III, could be preceded by proton transfer from peroxide to carboxylate oxygen (general base catalysis) concerted with peroxy oxygen attack on phosphorus:
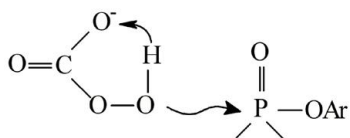
Richardson et al. [8], in discussing these systems, point out that proton transfer could involve a solvent molecule (water or alcohol):
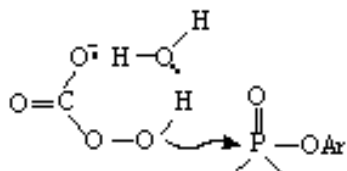
Regardless of the detailed mechanism of dephosphonylation by HCO_4^- the data point in the Bronsted relationship (fig. 2) involves the pK_a for deprotonation of the carboxylic, rather than the hydroperoxy

group, and the fit in this relationship apparently involves cancellation of effects in hydrogen and oxygen transfers. There is uncertainty in the extent of contribution of reaction with HCO_4^- which in some conditions is small, and the value of k_{Nu} is uncertain (equation (15)), and lower than expected (fig. 2). The low slope of the Bronsted plot for these α-nucleophiles also obscures deviations from the line plotted for other nucleophiles which, except for HO_2^-, have no readily exchangeable hydrogen and do not involve the cancellations noted earlier.

CONCLUSIONS. Dephosphorylation kinetics of NPDEPN in $H_2O_2/NH_4HCO_3/HO^-$ show that HCO_4^- and CO_4^{2-} are efficient α-nucleophiles, more reactive by several orders of magnitude than "normal" anionic oxygen nucleophiles of similar basicities. Of all known inorganic anionic α-nucleophiles HCO_4^- ion has the lowest basicity (pK_a =3.45). Intramolecular general acid-base catalysis appears to be a factor in the abnormally high reactivity of the peroxyhydrocarbonate ion.

РЕЗЮМЕ. С целью поиска новых высокореакционноспособных α-нуклеофилов изучена кинетика разложения 4-нитрофенилдиэтилфосфоната (NPDEPN) системой $H_2O_2/NH_4HCO_3/HO^-$ (pH 7.7—10.4). Данная система генерирует ионы HCO_4^- и CO_4^{2-}; с использованием соответствующих констант равновесия были рассчитаны равновесные концентрации этих ионов, что дало возможность определить константы скорости второго порядка их нуклеофильных реакций с NPDEPN, $k_{HCO_4^-}$= =0.006 и $k_{CO_4^{2-}}$=0.18 $M^{-1} \cdot c^{-1}$ (25 °C, μ=2.0 M). Сопоставление в рамках уравнения Бренстеда полученных величин и констант k для других неорганических анионов в реакции с NPDEPN позволило отнести ионы HCO_4^- и CO_4^{2-} к типичным α-нуклеофилам. Результаты могут иметь значение для выбора оптимальных условий разложения экотоксикантов различной природы.

РЕЗЮМЕ. З метою пошуку нових високореакційноздатних α-нуклеофілів вивчено кінетику розкладу 4-нітрофенілдіетилфосфонату (NPDEPN) системою $H_2O_2/NH_4HCO_3/HO^-$ (pH 7.7—10.4). Дана система генерує йони HCO_4^- і CO_4^{2-}; з використанням відповідних констант рівноваги було обчислено рівноважні концентрації цих йонів, що дало змогу визначити константи швидкості другого порядку їх нуклеофільних реакцій з NPDEPN, $k_{HCO_4^-}$=0.006 і $k_{CO_4^{2-}}$=0.18 $M^{-1} \cdot c^{-1}$ (25 °C, μ= =2.0 M). Зіставлення в рамках рівняння Бренстеда одержаних величин і констант k для інших неорганічних аніонів у реакції з NPDEPN дозволило вважати йони HCO_4^- і CO_4^{2-} типовими α-нуклеофілами. Результати можуть мати значення для вибору оптимальних умов розкладу екотоксикантів різної природи.

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