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Synergism in Liquid/Solid Phase-transfer Catalysis

Vera A. Savyolova, Lyubov N. Vakhitova,* Aleksandr N. Magasinski, Vladimira V. Rybak and Boris V. Panchenko

L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, 340114 Donetsk, Ukraine. Fax: +7 0622 553 542

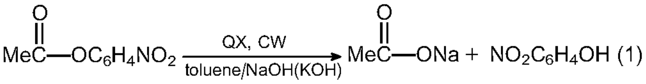
Powerful synergism in the hydrolysis reaction of *p*-nitrophenyl acetate in a liquid/solid system in the presence of the catalytic couple quaternary onium salt/crown ether has been detected.

Although the synergism effect for catalytic systems with more than one catalyst is widely known for homo- and heterogeneous catalysis, information on this phenomenon under phase-transfer catalysis conditions is concerned mainly with the rate acceleration on adding various organic and inorganic compounds which are not themselves interfacial catalysts.[1–6] There are only a few reports on the use of mixtures of crown ethers with quaternary ammonium salts in interfacial reactions.[7–10] In the works cited no quantitative assessment of the effect of a catalyst mixture with reference to that expected for additive action of the catalytic couple has been reported.

In order for such an assessment to be made, the reaction kinetics of the interaction of *p*-nitrophenyl acetate **1** with solid sodium and potassium hydroxides was studied in the presence of onium salts QX **2** and crown ethers CW **3**, both individually and in combination, with stirring (400 rpm) in toluene at 25 °C. [QX: **a**, Et_4NBr; **b**, $Me_3C_{16}H_{33}NBr$; CW: **a**, 18-crown-6; **b**, dibenzo-18-crown-6].

All kinetic experiments were carried out using freshly-ground (ball vibrating mill, particle size $20+10$ μm) Lachema sodium and potassium hydroxides (NaOH 95%, carbonates 0.2%, H_2O 3.3%; KOH 84%, carbonates 4.4%, H_2O 11.6%). Special experiments showed that, notwithstanding the fact that the presence of moisture in alkali influences the results, the data obtained are reproducible with an accuracy of 5–10% when employing one batch of the alkali hydroxides.

Under equimolar reagent concentrations the hydrolysis reactions proceed in accordance with reaction (1).



$$\mathrm{MeC(=O)-OC_6H_4NO_2} \xrightarrow[\text{toluene/NaOH(KOH)}]{\text{QX, CW}} \mathrm{MeC(=O)-ONa} + \mathrm{NO_2C_6H_4OH} \quad (1)$$

Reaction rates under pseudo-first order conditions with respect to ester **1**, both in a two-phase system (k/s^{-1}) and in an organic phase ($k^{\mathrm{org}}/\mathrm{s}^{-1}$) were followed spectrophotometrically by measuring the absorbance of liberated *p*-nitrophenolate ion at 410 nm in the bulk organic solvent.

The samples were withdrawn from the two-phase system by means of a special tube tipped with porous glass filter. Under the experimental conditions practically the whole of the phenol (>98%) was in the form of phenolate ion in the organic phase.

The apparent pseudo-first order rate constants for reactions in the two-phase system (k) and in the organic phase (k^{org}) remained practically constant during the course of the process. The difference in magnitude between these constants was taken to be a measure of the reaction rate at the interface ($k^{\mathrm{int}}/\mathrm{s}^{-1}$):

$$k^{\mathrm{int}} = k - k^{\mathrm{org}} \qquad (2)$$

The data in Table 1 for reaction (1) in the toluene/solid phase system in the presence of catalysts **2a** and **3b** show that the reaction occurs predominantly at the interface. An extraction mechanism is achieved only for those systems with potassium hydroxide in which the water content constitutes 11.6%, and always in combination with interfacial ones. Taking into account the dominant role of water in the reactions studied it may be postulated that in an interfacial regime the reaction proceeds in a so-called "omega-phase"[11] between the solid surface and toluene.

The influence of catalyst mixtures in the toluene/NaOH system was demonstrated with reaction (1) proceeding within the interfacial regime ($k = k^{\mathrm{int}}$). The dependence of apparent

Table 1 Rate constants for the reaction (1) (QX = **2a**, CW = **3b**) in the toluene/solid phase system[a] at 25 °C; [**1**] = 2.5×10^{-4} M.

Nucleophile	Catalyst	$c/10^{-3}$ mol dm^{-3} [b]	$k^{\mathrm{int}}/10^{-3}$ s^{-1}	$k^{\mathrm{org}}/10^{-3}$ s^{-1}
NaOH	**2a**	25	0.04 ± 0.01	no reaction
(3.3% H_2O)	**3b**	25	0.40 ± 0.08	no reaction
KOH	**2a**	25	0.22 ± 0.04	0.24 ± 0.02
(11.6% H_2O)	**3b**	25	0.79 ± 0.10	0.30 ± 0.07
KOH (5% H_2O)	**3b**	25	2.24 ± 0.23	no reaction

[a] Solid phase: 0.056 g (1 mmol) KOH and 0.04 g (1 mmol) NaOH in 40 ml of toluene. [b] Catalyst concentration.

pseudo-first order rate constants upon the concentration of catalysts **2a** (k_{QX}) and **3a** (k_{CW}) is plotted in Fig. 1 (curves 1 and 2, respectively). For the additive action of a catalytic mixture of QX and CW equation (3) is valid.

$$k_{ad} = k_{QX} + k_{CW} \tag{3}$$

The experimental k values for catalytic couples studied show that the rate is increased by:

$$k = k - k_{ad} \tag{4}$$

The dependence of Δk on molar fraction of a catalyst in the mixture is indicative of synergism (Fig. 1, curve 3).

As a quantitative measure of the synergic ability of the catalyst couple we propose to use the parameter S:

$$S = \frac{k}{k_{ad}} \tag{5}$$

The calculation of synergic-ability parameter S according to equation (5) for the reaction (1) shows that the rate increment is 21 times as large as that expected for additive action of catalytic couple, *i.e.* the acceleration amounts to 2100%.

Most likely, such a powerful synergic effect results from the favourable orientation of reagents and catalysts in a pre-reactive complex at the interface. The role of the crown ether consists of activation of the OH^- anion through complex formation with the Na^+ cation, while the quaternary onium cation facilitates OH^- "release" from the crystal lattice followed by OH^- transfer to the reaction site.

We suggest that the introduction of such a protic additive as methanol, which is miscible with both water and toluene, causes disruption of the omega-phase and hence the qualitative and quantitative changes in reactivity.

Addition of methanol to the system containing the catalytic couple (**2a** + **3a**) gives rise to the following effects (Table 2): i, a change in the topology of the process from an interfacial to an extraction-interfacial mechanism, the contribution of the former decreasing with increasing protic additive concentration (*cf.* k^{int}/k^{org}); ii, synergism for the reaction in organic phase (S^{org}) is substantially weaker than that for the reaction at the interface (S^{int}); iii, synergism drops rapidly as the concentration of protic additive increases so that for the reaction in organic phase at $V_{MeOH} = 0.06$ ml a diminution rather than an increase in reaction rate is observed (antagonism, S value is negative in sign). Data in Table 2 for the catalytic couple (**2a** + **3a**) provide sufficient reason to postulate that the most significant synergism effect occurs for reaction at the interface, most likely in the omega-phase.

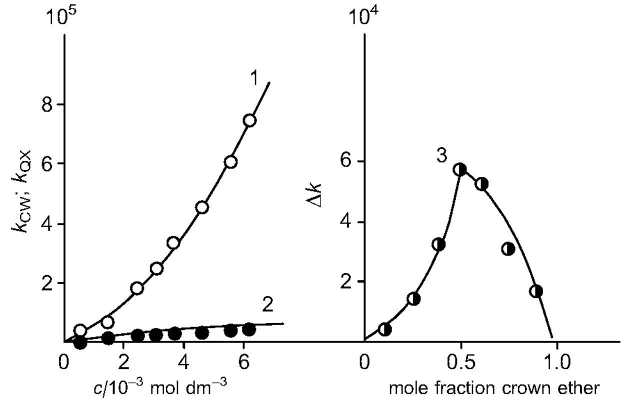


Fig. 1 Observed pseudo-first order rate constants for the reaction of *p*-nitrophenyl acetate with alkali in the system toluene/NaOH at 25 °C as a function of concentration of 18-crown-6 (k_{CW}, 1) and tetraethylammonium bromide (k_{QX}, 2); plot of the rate increment Δk (3) as a function of mole fraction of catalyst in the mixture {0.01 g (0.25 mmol) NaOH per 40 ml toluene; [**1**] = 5×10^{-5} mol dm^{-3}; [**2a**]+[**3a**] = 6.25×10^{-3} mol dm^{-3}}.

Table 2 Synergic ability parameters for the reaction (1) in the presence of a mixture of catalysts QX **2a,b** and 18-crown-6 **3a** in the toluene/NaOH system[a] with addition of methanol (V_{MeOH}) at 25 °C.

Catalytic couple	V_{MeOH}/ml	$\frac{k^{int}}{k^{org}}$	Synergic ability parameter		
			S^{org}	S	S^{int}
2a + **3a**	0	$\gg 10^b$	no reaction	20.4	20.4
	0.02	6.2	0.8	3.4	4.8
	0.04	3.0	0.3	2.6	7.6
	0.06	3.0	–0.5	0.1	0.6
2b + **3a**	0	[c]	no reaction	[c]	[c]
	0.02	6.5	–0.6	0.1	0.1
	0.04	0.71	–0.5	–0.5	–0.4
	0.06	0.63	–0.5	–0.6	–0.7

[a] Reaction conditions: 0.01 (0.25 mmol) NaOH in 40 ml toluene; reagent concentrations in toluene, M: [**1**] = 5×10^{-5}, [QX] + [CW] = 6.25×10^{-3} and [QX] = [CW] = 3.125×10^{-3} mol dm^{-3}. [b] The lower limit of the ratio estimated on the assumption that less than 10% of the overall rate is due to the reaction in organic phase and is within the limits of experimental error. [c] An attempt to determine the reaction rate was unsuccessful because of *p*-nitrophenolate anion sorption at the solid phase.

In our opinion, a quaternary ammonium salt like **2b** (with a lypophilic cation) should have a substantial effect on the properties of the omega-phase. Indeed, substitution of **2b** for **2a** in a catalytic couple with crown ether **3a** gives rise to a qualitative change in catalytic behaviour (Table 2), namely, the synergism not only fails to reveal itself in catalysis by the couple (**2b** + **3a**) but a pronounced antagonism is observed both for the reaction in the organic phase and at the interface, although in the latter case this effect shows up somewhat weakly, especially with minor amounts of added methanol.

The data presented therefore demonstrate conclusively the high efficiency of a catalytic mixture of crown-ether and quaternary ammonium salt involving weakly lypophilic cation that should be exhibited in an aprotic solvent/solid system for phase-transfer reactions catalysed by an interfacial mechanism.

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