## Kinetic Study of the Reaction of Triphenylphosphine with Acrylic Acid in Alcohol Media

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**Abstract**—Kinetic study of the reaction of triphenylphosphine with acrylic acid in alcohol media was carried out by spectrophotometric method. Use of alcohols as solvents is shown to introduce a specific feature in the kinetic picture of the reaction due to the appearance of parallel channels of proton transfer: from alcohol and from another molecule of acrylic acid in the solution.

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The unique reactivity of the tertiary phosphines as compared to their closest analogs, amines, led in recent decades to the discovery of a huge number of new reactions of activated alkenes, alkynes and allenes in which phosphines act as nucleophilic catalysts [1]. Most of these transformations include the processes of proton transfer, which, according to the latest experimental and theoretical studies [2, 3], may limit the whole reaction rate, or require the participation of a third molecule, the proton donor. While studying the mechanism of the quaternization of tertiary phosphines with unsaturated carboxylic acids, we recently reported the results of kinetic studies of these reactions in acetic acid [4] and also concluded that the process of proton transfer in the reaction course takes place not spontaneously, but only with the participation of solvent molecules, and it limits the whole process rate. The substrate carboxy group shows no specific effect on the reaction course. Quaternization of phosphine in all cases is described by the third order kinetic equation (1), which, in addition to the concentration of reactants, includes the concentration of acetic acid as the protonating reagent.

$$W = k_{\rm H}C_{\rm p}C_{\rm c} = k_{\rm HI}C_{\rm s}C_{\rm p}C_{\rm c}.$$
 (1)

Here,  $C_c$  is the concentration of unsaturated carboxylic acids,  $C_p$  is the concentration of phosphine,  $C_s$  is the concentration of the solvent (acetic acid),  $k_{\rm II}$  and  $k_{\rm III}$  are respectively the second and third order rate constants.

We thought it interesting to see how the replacement of the solvent with strong acidic properties, acetic acid, by an alcohol, which is less prone to release proton, will affect the reaction mechanism. Here we report on the results of kinetic study of the reaction of triphenylphosphine with acrylic acid in a series of alcohols.

Ph<sub>3</sub>P + CH<sub>2</sub>=CH - COOH  

$$\rightarrow$$
 Ph<sub>3</sub>P - CH<sub>2</sub> - CH<sub>2</sub> - COO<sup>-</sup>,  
R = Me, Et, Pr, *i*-Pr, Bu, *s*-Bu, *i*-Bu, *t*-Bu.

Note that such a study we have already initiated earlier for itaconic acid [5], but the use of just acrylic acid for the same purpose was the best because it combines several important features: high reactivity, second only to maleic acid (as found previously [4]), the presence in the molecule of only one carboxy group, which does not complicate the kinetic picture of the reaction due to the possible emergence of parallel channels of proton transfer, and the lack of restrictions on the solubility in the selected solvents.

Use of alcohol medium to study the kinetics of reaction of triphenylphosphine with acrylic acid led to a complication of the kinetic pattern: In all cases the first order of the reaction was revealed with respect to triphenylphosphine and a fractional, greater than unity, order with the respect to acrylic acid. Therewith, a dependence was observed of the reaction order with respect to the acid on its concentration in solution. A trend was also traced in the change of order (*n*) toward acrylic acid in the range of  $C_c$  from 0.03 to 0.5 M: it is

closest to unity in the primary alcohols, differs significantly from unity in secondary alcohols, and differs considerably in a tertiary alcohol.

Since a similar situation was observed formerly for the reaction of triphenylphosphine with itaconic acid [5], we assumed that in this case also there are two parallel channels for the proton transfer, one of which is of first order with respect to the acid, and the other is of the second order. The kinetic equation of the reaction is then given by Eq. (2).

$$W = k_{\rm II}C_{\rm p}C_{\rm c}k_{\rm III}C_{\rm p}C_{\rm c}^{2} + = (k_{\rm II}C_{\rm c} + k_{\rm III}C_{\rm c}^{2})C_{\rm p} = k'C_{\rm p}.$$
 (2)

Here  $k' = k_{II}C_c + k_{III}C_c^2$  is pseudo-first order "effective" rate constant at  $C_c >> C_p$ , observed in the kinetic experiment.

The rate constants  $k_{\text{II}}$  and  $k_{\text{III}}$  in this case can be determined from Eq. (3), which is linear with the concentration of acrylic acid.

$$k'/C_{\rm c} = k_{\rm II} + k_{\rm III}C_{\rm c}.$$
 (3)

High quality of the obtained linear dependences (Fig. 1) is a criterion of validity of the approach used to expand the effective rate constant over the elementary components and the reliability of the determination on this basis of the rate constants  $k_{\text{II}}$  and  $k_{\text{III}}$ .

The nature of the constant  $k_{\text{III}}$  is clear: It unambiguously describes the process of proton transfer from a second molecule of acrylic acid. But with respect to the constant  $k_{\text{II}}$  there are two alternatives: (1)  $k_{\text{II}}$  reflects the intramolecular proton transfer from attacked acid molecule through the transition state of type **A**:



(2) As in the case of acetic acid [4],  $k_{\rm II}$  reflects the intermolecular proton transfer from solvent. The result is a superposition of two channels of proton transfer to the carbanion center of the attacked substrate: from alcohol, a weak acidic reagent, but contained in the solution in a high concentration as a solvent, and from



Fig. 1. Separation of  $k_{\rm II}$  and  $k_{\rm III}$  rate constants for the reaction of triphenylphosphine with acrylic acid (30°C) in: (1) MeOH:  $k'/C_{\rm c} = 2.1 \times 10^{-3} C_{\rm c} + 4.3 \times 10^{-3}$ , R = 0.9984; (2) EtOH:  $k'/C_{\rm c} = 1.8 \times 10^{-3}C_{\rm c} + 1.9 \times 10^{-3}$ , R = 0.9987; (3) PrOH:  $k'/C_{\rm c} = 2.3 \times 10^{-3}C_{\rm c} + 1.4 \times 10^{-3}$ , R = 0.9997; (4) *i*-PrOH:  $k'/C_{\rm c} = 1.7 \times 10^{-3}C_{\rm c} + 0.7 \times 10^{-3}$ , R = 0.9994; (5) BuOH:  $k'/C_{\rm c} = 1.6 \times 10^{-3}C_{\rm c} + 0.6 \times 10^{-3}$ , R = 0.9989; (6) *s*-BuOH:  $k'/C_{\rm c} = 3.6 \times 10^{-3}C_{\rm c} + 0.6 \times 10^{-3}$ , R = 0.9981; (7) *i*-BuOH:  $k'/C_{\rm c} = 3.6 \times 10^{-3}C_{\rm c} + 0.1 \times 10^{-3}$ , R = 0.9992; and (8) *t*-BuOH:  $k'/C_{\rm c} = 1.2 \times 10^{-3}C_{\rm c} + 0.1 \times 10^{-3}$ , R = 0.9986.

acrylic acid, whose proton-donor properties are significantly higher, but its concentration is much lower.

The contribution of each channel of proton transfer into the effective rate constant influences the observed value of the order of the reaction with respect to the acid, which generally ranges from one to two, and leads to the above-noted trends in its change.

In favor of the latter option (intermolecular proton transfer involving alcohol solvent) indicates the variation of constants  $k_{II}$  in parallel with the change in acidity in the series of alcohols. Furthermore, there is a good correlation between the corresponding values of log  $k_{II}$  and  $pK_a$  of alcohols (Fig. 2, curve 1).

$$\log k_{\text{II}} = -0.435 \text{pK}_{\text{a}} + 4.253,$$
  
N = 5, R = 0.990, s = 1.01×10<sup>-2</sup>.

Clearly, the parameter  $pK_a$ , being the most common indicator of acid properties of the solvent, is by no means universal and does not describe the totality of the solvent effect on the reaction rate. Thus, the attempt to include in this correlation acetic acid that differs substantially in its properties (not only the proton-donor ones) from alcohol reduces its quality significantly:

$$\log k_{\rm II} = -0.197 p K_{\rm a} + 0.247,$$
  
N = 6, R = 0.95, s + 1.26×10<sup>-1</sup>.



**Fig. 2.** Correlation between the values: (1) log  $k_{\text{II}}$ , (2) log  $k_{\text{s}}$  and  $pK_{\text{a}}$  of alcohol in the reaction of triphenylphosphine with acrylic acid.

Using the parameter  $pK_a$  for a series of related compounds (alcohols) is reasonable, and it yields, of course, much better linearity.

For a more detailed study of the issue concerning the role of alcohol in the quaternization of triphenylphosphine by acrylic acid for three rather high-boiling alcohols (PrOH, BuOH, and *i*-BuOH), we performed a separation of the rate constants using Eq. (3) for different temperatures. The high quality of the obtained isokinetic dependence

$$\log k (50^{\circ}\text{C}) - \log k (20^{\circ}\text{C}) \tag{4}$$

indicates that both the above channels of proton transfer in alcohols are isokinetic, that is, are of common nature, and therefore reflect the intermolecular proton transfer from the medium.

$$\log k(50^{\circ}\text{C}) = 0.926 \log k(20^{\circ}\text{C}) + 0.539,$$
  
N = 6, R = 0.993, s =6.11×10<sup>-4</sup>.

In this case, the determined second-order rate constants are latent intermolecular in nature and include the alcohol concentration [Eq. (5)] that must be

The rate constants  $k_s$  and  $k_c$  for the reaction of triphenylphosphine with acrylic acid in alcohols ROH (30°C)

R	<i>C</i> <sub>s</sub> , M	С₀, М	$k_{\rm s} \times 10^3$ , $l^2 {\rm mol}^{-2} {\rm s}^{-1}$	$k_{\rm c} \times 10^3$ , $l^2 {\rm mol}^{-2} {\rm s}^{-1}$
Me	24.4	2.05	0.18	2.1
Et	17.0	1.06	0.11	1.8
Pr	13.3	0.61	0.11	2.3
<i>i</i> -Pr	13.0	0.41	0.054	1.7
Bu	10.8	0.48	0.11	2.5
s-Bu	10.8	0.38	0.056	1.6
<i>i</i> -Bu	10.7	0.47	0.16	3.6
<i>t</i> -Bu	10.5	0.08	0.0095	1.2



Fig. 3. Common isokinetic dependence log  $k(50^{\circ}C)$ -log  $k(20^{\circ}C)$  for the reaction of triphenylphosphine with acrylic acid in alcohols and carboxylic acids.

taken into account, in particular, in the calculation of the activation entropy.

$$k_{\rm II} = k_{\rm s} C_{\rm s}.$$
 (5)

Here,  $k_s$  is the third-order rate constant describing the proton transfer from the solvent,  $C_s$  is the concentration of solvent (alcohol). The third-order rate constant describing the proton transfer from the second molecule of acrylic acid we denote as  $k_c$ , that is,  $k_c = k_{III}$ .

Note that in the isokinetic relationship (4), along with the constants  $k_c$  can be used also the constants  $k_{II}$  without reducing them to the constants  $k_s$  according to Eq. (5) independent of alcohol concentration, as the latter are directly proportional, and the change in  $C_s$  within the operating temperature range can be neglected, by considering it a constant value.

The  $k_s$  constants (see the table), "purified" from the influence of solvent concentration, correlate with the values of p $K_a$  of alcohol better than  $k_{II}$  (Fig. 2, plot 2).

$$\log k_{\rm s} = -0.355 \text{pK}_{\rm a} + 1.752,$$
  
N = 5, R = 0.996, s = 2.55×10<sup>-3</sup>.

The effect of alcohol on the nature of the rate constant  $k_c$  is more complicated (see the table), and to identify any correlation is difficult owing to the relatively narrow range of their changes. However, it is of some interest to consider the value  $k_{II}/k_{III} = k_s C_s/k_c = C_0$ , that is a constant for each alcohol in the concentration units. Its physical meaning becomes clear from the kinetic Eq. (2):  $C_0$  is a concentration of acrylic acid providing equal rates of proton transfer through both channels. Obviously, the  $C_0$  is smaller when the alcohol acidity is lower, that is, lower its tendency to release proton in the course of reaction (see the table).

Activation parameters of the studied reactions (subscripts correspond to the channels of the proton transfer) in various alcohols are given below. The closeness of the values of activation parameters of the two reaction channels in each alcohol determines a possibility of their parallel course. The large negative activation entropy indicates a high ordering of the activated reaction complex.

R	Pr	Bu	<i>i</i> -Bu
$\Delta H_{\rm s}^{\neq}$ , kcal mol <sup>-1</sup>	10.7	10.0	10.2
$-\Delta S_{\rm s}^{\neq}$ , eu	41	44	42
$\Delta H_{\rm c}^{\neq}$ , kcal mol <sup>-1</sup>	10.8	9.9	9.9
$-\Delta S_{\rm c}^{\neq}$ , eu	35	38	37

If the above interpretation of the established isokinetic relationship (4) is true, then should be a general correlation with the previously used other solvent, acetic acid, in which the proton transfer also occurs from the environment and the protonating agent is the acetic acid. This assumption is fully confirmed by the high quality of the corresponding general correlation.

$$\log k(50^{\circ}\text{C}) = 0.931 \log k(20^{\circ}\text{C}) + 0.554, \quad (6)$$
$$N = 7, R = 0.9996, s = 4.90 \times 10^{-4}.$$

In addition to acetic acid, we also studied the kinetics of the reaction of triphenylphosphine with acrylic acid in the medium of propionic acid. In this case, as expected, the reaction is of first order toward each reactant, and by analogy with acetic acid can be assumed that the reaction kinetic equation (1) is also true, and proton transfer occurs from the solvent. Kinetic and activation parameters of this reaction in comparison with acetic acid [4] are listed below. In propionic acid the reaction rate is reduced, but the general trend of the reaction acceleration in a carboxylic acid medium persists.

R	Me	Et
$k_{\rm III} \times 10^3$ , $l^2  {\rm mol}^{-2}  {\rm s}^{-1}  (30^{\circ}{\rm C})$	8.18	3.32
$\Delta H^{\neq}$ , kcal mol <sup>-1</sup>	8.5	9.9
$-\Delta S^{\neq}$ , eu	40	37

If the above conclusions about the mechanism of the reaction in propionic acid are correct, the kinetic parameters of this reaction should obey the overall isokinetic relationship (6), which in fact is observed (Fig. 3).

log 
$$k(50^{\circ}\text{C}) = 0.943 \log k (20^{\circ}\text{C}) + 0.593$$
  
 $N = 8, R = 0.9994, s = 7.66 \times 10^{-4}.$ 

So, we found a common isokinetic relationship for the reaction of triphenylphosphine with acrylic acid in alcohols and carboxylic acids. It is identical with the isokinetic dependence found for a series of unsaturated carboxylic acids [4], which confirms the general character of the previously proposed stepwise mechanism of their reaction with tertiary phosphines regardless of the solvent nature.



According to this mechanism, the proton migration to the carbanion center of the pre-reaction complex **B** generated as a result of the nucleophilic attack of phosphine, always occurs at the expense of an external proton donor, the solvent or a second molecule of the unsaturated acids, and it limits the whole process rate. Thus, the study allowed us to establish that the reaction of triphenylphosphine with acrylic acid in alcohols is described by more complex, as compared to carboxylic acids, kinetic equation of the form (2) with two parallel channels of proton transfer, both of which are intermolecular. Proton transfer in alcohols

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 80 No. 9 2010

proceeds with either direct participation of solvent molecules, or involves a second molecule of acrylic acid, while in the medium of strong proton donor carboxylic acids it proceeds through the solvent only. Both the possible channel of the proton migration (through the solvent, or through second molecule of unsaturated acid) obey the same general isokinetic dependence, which reflects retaining of the main features of the reaction mechanism and structure of the activated complex, regardless of the nature of the specific proton donor in the final act of the reaction.

## **EXPERIMENTAL**

Investigations were carried out spectrophotometrically on a Perkin Elmer Lambda 35 instrument with a temperature-controlled cell (temperature control accuracy  $\pm 0.1^{\circ}$ C) in the media of the respective solvents at a wavelength 300 nm (for alcohol) or 290 nm (for propionic acid) under conditions of pseudo-first order with respect to triphenylphosphine and at a large excessive concentration of acrylic acid, which ranged from 0.03 to 0.55 M. The thickness of the transmitting layer was 1 cm. Kinetic measurements were carried out at temperatures from 20 to 50°C. The pseudo-first order rate constants were determined from the decrease in optical density of the absorption band of triphenylphosphine in the reaction mixture, calculating by the least squares method the slope of the anamorphosis of the kinetic curve in the coordinates log  $(D_x - D_\infty) - t$ , where  $D_x$  is current optical density,  $D_{\infty}$  is the final optical density upon completion of the reaction. t is time. The true rate constants in alcohols were determined as described in the main text. The third order rate constant in propionic acid was determined by dividing the rate constant of the pseudofirst order by the concentration of excess reagent and the concentration of EtCOOH. Concentrations of solvents were taken constant and were calculated with the formula  $C_s = d_{30}/M$ . The values of  $d_{30}$ , as well as the  $pK_a$  of solvents were taken from [6]. Activation parameters were calculated from the temperature dependence of the third order rate constant using the known formulas [7].

The test solutions were prepared in the working cell by mixing the reagent solutions of known concentration at a given temperature in required amounts, stirring and placing the mixture in a temperaturecontrolled spectrophotometer cell. At this moment the time countdown and photometry began. Kinetic measurements were repeated in all cases at least three times. The error in determining the rate constants does not exceed  $\pm$  5%.

The initial reagents (triphenylphosphine and acrylic acid) and solvents were commercial products subjected to additional purification by known methods [6–8]. The purity of solvents was checked by the absence of changes in the spectra of prepared solutions of the starting substances within 1 day.

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