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Kinetics and Mechanism of Triphenylphosphine Quarternization with Unsaturated Carboxylic Acids in the Medium of Acetic Acid

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Abstract—Kinetics of reaction of triphenylphosphine with a series of unsaturated carboxylic acids and related esters in the medium of acetic acid as well as in mixtures of acetic acid and acetonitrile was studied by spectrophotometry. The data obtained show that the process of quarternization should be described by kinetic equation of third order, the proton transfer occurs from the solvent. A stepwise mechanism of interaction including formation of prereaction complex on the reaction pathway is proposed.

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Reactions of tertiary phosphines with unsaturated electrophilic reagents are widely used in modern organic synthesis for obtaining practically applicable compounds [1, 2]. Our group performs systematic investigation in this field of reactions of tertiary phosphines with unsaturated carboxylic acids [3–7]. Related data have been published only sporadically [8–10]. Paying attention not only to synthetic problems but also to the respective problem of reaction mechanism we have initiated study of kinetics of this reaction and established that there are alternative canals of proton transfer depending on the nature of solvent and of the initial unsaturated carboxylic acid [6, 7]. This leads to realization of kinetic equations of second (1) or third (2) order or to their superposition (3):

$$W = k_{\mathrm{II}} C_{\mathrm{PPh_3}} C_{\mathrm{uns}}, \tag{1}$$

$$W = k_{\mathrm{III}} C_{\mathrm{PPh_3}} C^2_{\mathrm{uns}}, \tag{2}$$

$$W = k_{\mathrm{II}} C_{\mathrm{PPh_3}} C_{\mathrm{uns}} + k_{\mathrm{III}} C_{\mathrm{PPh_3}} C^2_{\mathrm{uns}}, \tag{3}$$

where C_{uns} is the concentration of unsaturated carboxylic acid, $C_{\mathrm{PPh_3}}$ is the concentration of phosphine, k_{II} and k_{III} are respectively second and third order reaction rate constants.

Although the results earlier obtained allowed to reveal important regularities in the process of quarternization of tertiary phosphines and to propose its most probable mechanism [6], many problems remained unclear and required detailed study with an extended series of unsaturated carboxylic acids. In this connection appeared a problem of a choice of an appropriate solvent, because, as we found, most of solvents commonly used in kinetic investigations could not be applied because of too low reaction rate. We succeeded to solve this problem by using acetic acid that has been applied as solvent in our study of reaction of triphenylphosphine with itaconic acid [7]. The increase in the reaction rate is achieved owing to the presence of labile acidic protons necessary for the protonation of carbanionic center. Application of acetic acid is advantageous in several aspects:

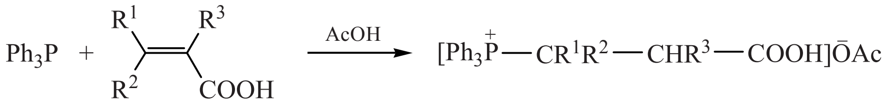
– To the reaction corresponds simple kinetic equation of type (1) regardless the substrate nature, that facilitates the obtaining of experimental results and their interpretation;

– High solvating ability of acetic acid toward unsaturated acids and phosphines of different structure;

– High boiling temperature that allows to perform kinetic measurements in a wide temperature range;

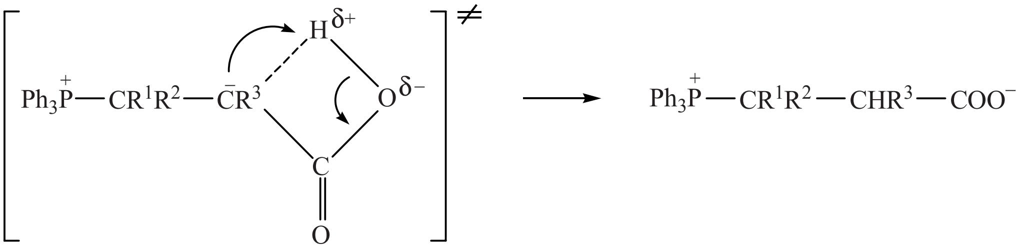
– Accessibility and ease of purification.

In this publication we report on the results of kinetic investigation of reactions of triphenylphosphine with acrylic (**I**), methacrylic (**II**), itaconic (**III**), crotonic (**IV**), maleic (**V**) and fumaric (**VI**) acids in the medium of acetic acid.

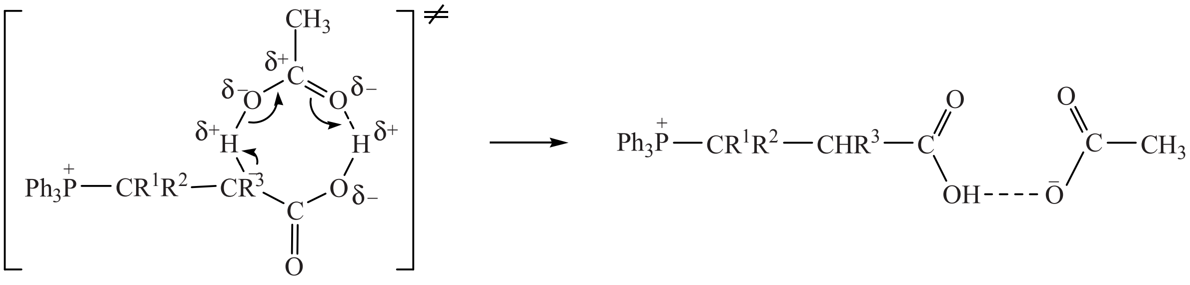


I: $R^1 = R^2 = R^3 = H$; **II**: $R^1 = R^2 = H$, $R^3 = CH_3$; **III**: $R^1 = R^2 = H$, $R^3 = CH_2COOH$; **IV**: $R^1 = CH_3$, $R^2 = R^3 = H$; **V**: $R^1 = R^3 = H$, $R^2 = COOH$; **VI**: $R^1 = COOH$, $R^2 = R^3 = H$.

As expectable, the phosphine quarternization in all the cases is described formally by second order kinetical Eq. (1) with first order in each reagent. However, application of acetic acid as a medium for these reactions inspires a question concerning the proton transfer in the activated complex: Whether the carboxylic group of unsaturated acid is involved in the process or its effect is reduced only to the polarization of the substrate C=C bond? It can be assumed that despite the presence in the solution of acetic acid the proton transfer can occur also from the carboxylic group of the attacked molecule of unsaturated acid either via four-membered ring **A** or via certain coordination of a molecule of acetic acid by carboxylic group near the reaction center by means of hydrogen bonding in eight-membered activated complex **B**.



A



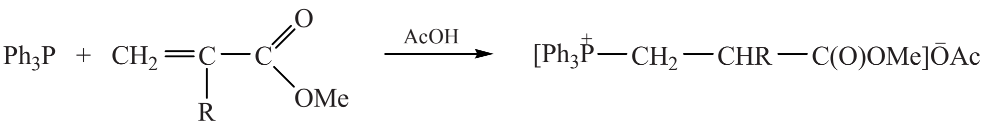
B

To clarify this situation that is important from the viewpoint of the reaction mechanism we carried out some additional investigations:

– kinetic study of reactions of triphenylphosphine with unsaturated carboxylic acid esters methyl acrylate **VII** and methyl methacrylate **VIII** in the acetic acid medium;

– kinetic study of reactions of triphenylphosphine with acrylic acid in the mixtures of acetonitrile with acetic acid.

The unsaturated esters **VII, VIII** contain C=C bond modeling that of unsaturated acid but do not contain carboxylic proton, thus transition states of **A** and **B** type become impossible.



VII: R = H; **VIII**: R = Me.

Reaction of tertiary phosphines with acrylates is well known [11]: in the absence of an appropriate proton-donor reagent the addition of phosphines is reversible, and they can initiate the polymerization. In the medium of acetic acid the carbanionic charge appearing at the attack by the phosphorus atom is neutralized by protonation, and the equilibrium is shifted toward phosphonium product. For this process the kinetic equation of type (1) formally is correct, but it should be taken into account that the concentration of acetic acid as protonating agent also should be included jnto the equation for the reaction rate (4).

$$W = k_{\mathrm{II}}C_{\mathrm{PPh_3}}C_{\mathrm{ester}} = k_{\mathrm{III}}C_{\mathrm{solv}}C_{\mathrm{PPh_3}}C_{\mathrm{ester}}, \tag{4}$$

where $k_{\mathrm{II}} = k_{\mathrm{III}}C_{\mathrm{solv}}$, C_{ester} is the concentration of ester, C_{solv} is the concentration of solvent (acetic acid).

It was interesting to compare the results of kinetic study of triphenylphosphine reactions with unsaturated carboxylic acids and with related ester. The isokinetic criterion log k_{II}(50°C) – log k_{II}(20°C) (Fig. 1) obtained at comparison of experimental rate constant at different temperatures attests undoubtedly that all the studied reactions belong to the same reaction series, that is, their mechanisms are of the same type.

$$\log k_{\mathrm{II}}(50°\mathrm{C}) = 0.9227\log k_{\mathrm{II}}(20°\mathrm{C}) + 0.5523,$$
$$N\ 8,\ \mathrm{R}\ 0.9997,\ s_0\ 3.24\times10^{-2}.$$

Hence, carboxylic group of unsaturated acid does not affect specifically the process of quarternization

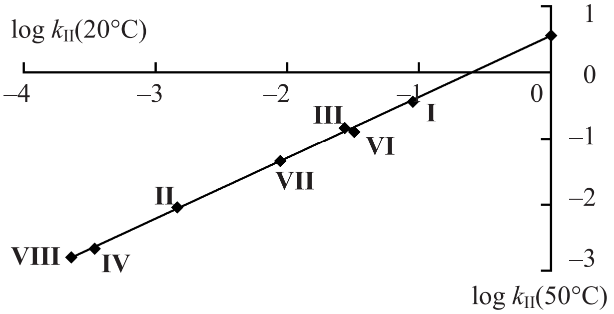
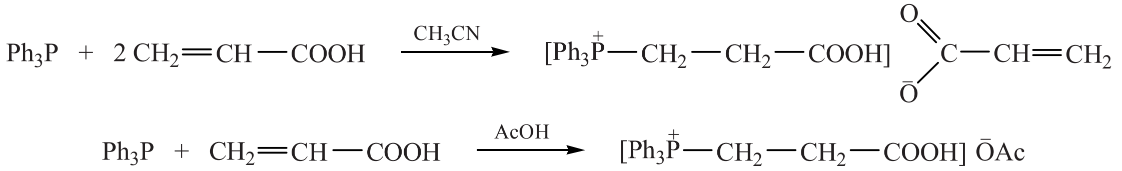


Fig. 1. Isokinetic plot log k_{II}(50°C)–log k_{II}(20°C) for the series of reactions of triphenylphosphine with unsaturated carboxylic acids and related esters.

and the hypothetical transition states **A** and **B** can be excluded.

Use of acetonitrile mixed with acetic acid as a solvent for the study of kinetics of triphenylphosphine reaction with acrylic acid allows to vary concentration of proton-donor reagent and thus to elucidate its contribution to the kinetic equation. It has been shown earlier [6] that in acetonitrile this reaction is described by kinetic Eq. (2) that is, of second order on acrylic acid. Adding acetic acid to the reaction mixture decreases the reaction order in acrylic acid to unity that indicates the change in the mode of proton transfer to the carbanionic center. While in aprotic acetonitrile the proton is transferred from the second molecule of acrylic acid, in the presence of acetic acid the latter bears the function of the protonating reagent.



$$\mathrm{Ph_3P + 2\,CH_2{=}CH{-}COOH \xrightarrow{CH_3CN} [Ph_3\overset{+}{P}{-}CH_2{-}CH_2{-}COOH]\ \bar{O}{-}C({=}O){-}CH{=}CH_2}$$

$$\mathrm{Ph_3P + CH_2{=}CH{-}COOH \xrightarrow{AcOH} [Ph_3\overset{+}{P}{-}CH_2{-}CH_2{-}COOH]\ \bar{O}Ac}$$

The experiment was arranged so as to provide inequality: $C_{\mathrm{uns}} \ll C_{\mathrm{solv}}$, that is, the concentration of unsaturated carboxylic acid was much less than that of solvent (acetic acid) permitting neglecting the proton transfer from the second substrate molecule. The plot of experimentally measured second order reaction rate constant on the mole fraction of acetic acid (x) is rather complicated (Fig. 2, *1*). With known concentration of acetic acid in the mixture it is possible with the equation $k_{\mathrm{II}} = k_{\mathrm{III}}C_{\mathrm{solv}}$ to calculate third order reaction rate constant which turned out to be connected linearly with the concentration of the acetic acid (Fig. 2, *2*).

$$k_{\mathrm{III}} = -0.0161x + 0.0244;\ N\ 6,\ \mathrm{R}\ 0.9825,\ s_0\ 1.08\times10^{-3}.$$

Since the constant k_{III} is “cleaned” from the effect of acetic acid concentration, it obviously reflects the effect of the latter as a component of medium rather than reagent, and the change in its concentration in the acetic acid–acetonitrile medium leads to changes in the polarity and other important properties of the mixed solvent.

The point for pure acetonitrile falls out of the plot because here the proton transfer occurs from the second molecule of unsaturated acid.

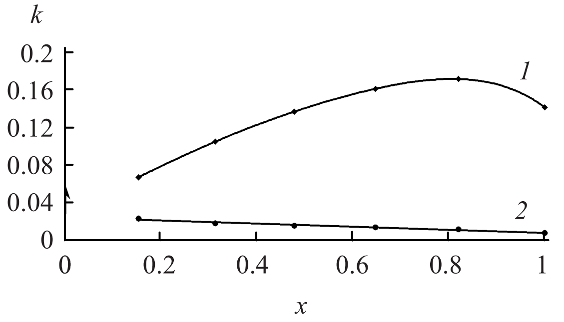


Fig. 2. The plots of reaction rate constants on the mole fraction of AcOH in the AcOH + MeCN mixture: (*1*) k_{II} and (*2*) k_{III}.

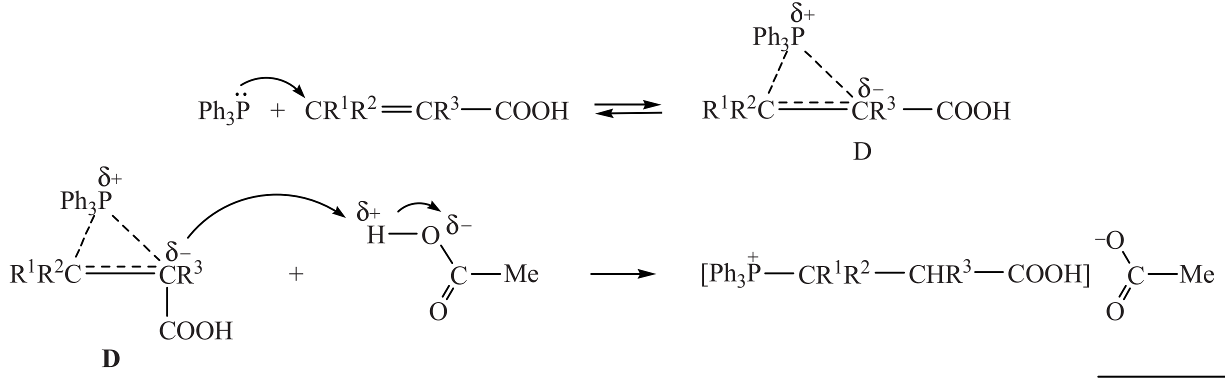
Thus, quarternization of triphenylphosphine with unsaturated carboxylic acids in the medium containing acetic acid is described by third order kinetic Eq. (5) and proceeds with proton transfer from the solvent.

$$W = k_{II}C_{PPh_3}C_{uns} = k_{III}C_{solv}C_{PPh_3}C_{uns.} \qquad (5)$$

The scope of obtained experimental observations points to a stepwise mechanism of reaction of tertiary phosphines with unsaturated carboxylic acids. Most probably the initial nucleophilic attack of the phosphine phosphorus atom on the electrophilic terminal carbon atom of the acid C=C generates prereaction complex of **D** type rather than zwitter-ionic intermediate of **C** type where strongly basic carbanionic center would be located near the acidic carboxylic group that is very doubtful. In the complex **D** the formation of a real covalent P–C with increase in phosphonium character of P atom and carbanionic character of C atom proceeds in parallel with the proton transfer on the generated carbanionic center. Therewith the protonation proceeds not by intramolecular mechanism which would lead instantly to the appearance of carboxylate phosphabetaine but from the medium by the action of another proton–donor reagent, the second molecule of unsaturated acid or solvent. The product of such interaction is the corresponding phosphonium salt.

$$Ph_3\overset{+}{P}—CR^1R^2—\overset{-}{C}R^3—COOH$$

C, Zwitter-ionic intermediate.



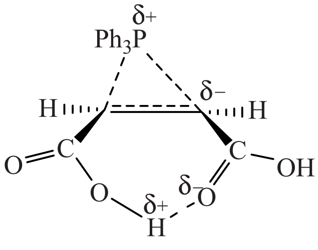
According to the kinetic data, the limiting step of the reaction is the step of proton transfer, because the kinetic equation includes concentration of the proton-donor alongside the concentrations of phosphine and unsaturated acid. This explains the fact of increase in the reaction rate of triphenylphosphine with unsaturated carboxylic acids in the acetic acid medium: as far as the proton transfer occurs from the solvent whose concentration is large, the experimentally measured second order reaction rate constant becomes also large.

The values of third order reaction rate constants and calculated respective values of activation parameters are listed in Table 1.

As seen from the table, the rate of triphenylphosphine quarternization depends considerably on the structure of the unsaturated carboxylic acid and varies by three orders of magnitude within the studied reaction series. In all likelihood, the character of the effect of the substituent at the C=C bond and the features of the whole process are determined by the nature of the prereaction complex **D** which has highly organized structure. Therefore the activation entropy which always is negative and high by absolute value contributes significantly to the energetics of these reactions.

The substituents both in α-and β-positions of the substrate decelerate conversion of carbon atoms from trigonal to tetragonal configuration, therefore the reactivity of substituted derivatives is always lower than that of unsubstituted ones (e.g., **II, III, IV** and other acids as compared with **I**, and **VII** as compared with **VIII**, see Table 1).

An exclusion is maleic acid reacting with notably higher rate than the other studied unsaturated carboxylic acids. Probably in this case the prereaction complex **D'** is additionally stabilized by a hydrogen bond between the neighboring carboxy groups.



D'

In the reaction with the isomeric fumaric acid such additional stabilization is impossible by steric reasons, and the reaction rate falls considerably.

Substituents in the β-position of the acid decrease the reaction rate due to screening the reaction center. Therewith, the proton-donor substituents **IV** diminish effective positive charge on the terminal carbon atom and thus retard attack by phosphine, while acceptor substituents promote reaction of **V, VI**. The character of substituent effect on the α-center is similar to that on β-center: donor substituents destabilize growing carbanionic charge of **II** while acceptors increase stability of the prereaction complex **D** (**III**).

Reactivity of esters is lower compared to the respective acids that is understandable for the ester groups exert weaker polarizing action on the C=C bond as compared with carboxy groups and as a consequence the double bond is characterized by lower electrophilicity, also the methoxycarbonyl group posseses a higher steric effect.

Thus, use of acetic acid as a medium for these reactions allowed us to extend considerably the reaction series of initial unsaturated carboxylic acids. The comparative kinetic investigation of triphenylphosphine reactions with unsaturated carboxylic acids and related esters showed the absence of principal difference in the mechanism of these reactions. The data obtained in this part of investigation in conjunction with the kinetic investigation of triphenylphosphine reaction with acrylic acid in the mixtures of acetic acid and acetonitrile suggest a stepwise mechanism of reaction of tertiary phosphines with unsaturated carboxylic acids that includes initial fast equilibrium formation of prereaction complex between the phosphine and C=C bond of the unsaturated substrate followed by relatively synchronous formation of real P–C covalent bond and proton transfer to the appearing carbanionic center. The proton transfer occurs from the medium with participation of proton-donor solvent, and it is the limiting step of the whole process.

Kinetic and activation parameters of triphenylphosphine reactions with unsaturated carboxylic acids and esters in acetic acid medium

Comp. no.	$k_{III}\times10^3$, l^2 mol^{-2} s^{-1} (30°C)	$\Delta H^{\neq}$, kcal mol^{-1}	$-\Delta S^{\neq}$, eu
I	8.18	8.5	40
II	0.16	10.8	40
III	2.87	9.9	38
IV	0.038	10.8	43
V	99.5	7.4	39
VI	3.12	8.2	43
VII	0.89	9.7	40
VIII	0.028	10.5	45

EXPERIMENTAL

Investigations were carried out by spectrophotometric method on a Perkin Elmer Lambda 35 instrument with thermostated cell (accuracy of the temperature control ±0.1ºC) in the medium of AcOH and mixtures of AcOH and MeCN, at the wavelength 290 nm, under conditions of pseudo-first order on triphenylphosphine and great excess of unsaturated acid or ester. The cell thickness 1 cm. The kinetic measurements were carried out in the temperature range from 20 to 50ºC. The rate constants were determined from the decrease in optical density of the triphenylphosphine absorption band in the reaction mixtures. The pseudo-first order rate constants were calculated by the least square method from the slope of the plot in the coordinates ln $(D_x - D_\infty) - t$, where D_x is the current optical density, D_∞ is the final optical density after reaction completing, t is time. The second order rate constants were calculated by dividing the pseudo-first order rate constant by concentration of the reagent taken in excess. The third order rate constants were calculated by dividing the second order rate constants by the AcOH concentration in the solution which in the absence of second solvent was taken as a constant, $C_{\text{solv}} = d_{30}/M = 17.3$ M [12]. The activation parameters were calculated from the temperature plots of the third order rate constants by commonly used formulas [13].

The studied solutions were prepared by mixing solutions of reagents with known concentrations in required amounts, at a given temperature, the mixture was stirred and placed to thermostated spectrophotometer cell, and this moment was taken as initial for time counting and photometry. Kinetic measurements in all the cases were made at least thrice. The rate constant error is not higher than ±5%.

The commercial initial reagents (triphenylphosphine, unsaturated carboxylic acids and esters) and solvents were additionally purified by known procedures [12–15]. The solvents purity was verified by the absence of changes in the spectra of the prepared solution during 24 h.

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