Heteroatom Chemistry
Volume 9, Number 7, 1998

Kinetics and Mechanism of the Unusual Insertion Reactions of Aryl Isocyanates into the C–C Bond of the Phosphonium Zwitter-Ion Derived by the Reaction of Triisopropylphosphine with Ethyl 2-Cyanoacrylate[1]

V. I. Galkin,* Yu. V. Bakhtiyarova, Yu. G. Gololobov,
N. A. Polezhaeva, and R. A. Cherkasov

Department of Chemistry, Kazan State University, Kazan, 42008, Russia

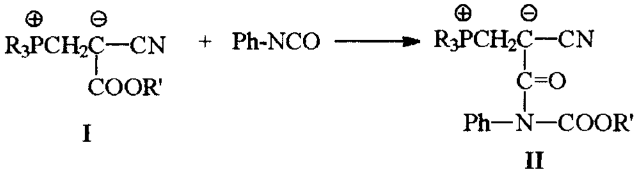
A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow 117813, Russia

Received 8 July 1998; revised 23 July 1998

ABSTRACT: *The kinetics of the reactions of aryl isocyanates with the zwitterion formed by the addition of triisopropylphosphine to ethyl 2-cyanoacrylate in acetonitrile solution have been determined by a spectrophotometric method. It was established that the reaction is second order overall, first order with respect to each of the reagents. A mechanism is proposed that consists of an attack of the carbanionoid center of the phosphabetaine on the carbonyl carbon atom of the isocyanate group and nucleophilic attack of the isocyanate nitrogen atom on the carbonyl carbon of the ester group, with rupture of the appropriate C-C bond, within the framework of a cyclic transition state.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 665–668, 1998

INTRODUCTION

Previously, an interesting reaction of phenyl isocyanate with the zwitter-ion, derived by the reaction of trialkylphosphines with alkyl 2-cyanoacrylates, has been reported [1]. This reaction was assumed to proceed by insertion of the isocyanate into the indicated C–C bond of the initially formed phosphabetaine **I**.



In the present work, the kinetics of this unusual reaction have been studied by spectrophotometry in a solution in acetonitrile at 20–60°C. It was established that the reaction is second order overall, first order with respect to each of the reagents. Rate constants and activation parameters are presented in Table 1.

A linear relationship of excellent quality in a plot of the activation parameters ΔS vs. ΔH Equation 1, Figure 1) was found and indicates that all the reactions studied belong to the same reaction series.

$$\Delta H^{\neq} = (40517 \pm 818) + (747 \pm 18)\,\Delta S^{\neq} \qquad (1)$$

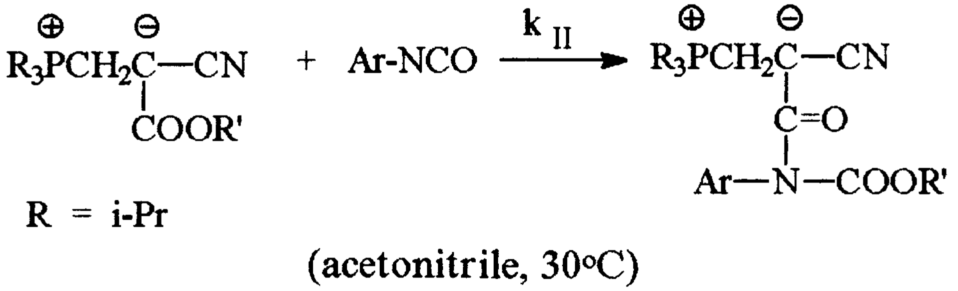
$$N = 5,\ R = 0.9995,\ S_o = 1.413$$

Correspondence to: V. I. Galkin.

Dedicated to Prof. Robert R. Holmes on the occasion of his 70th birthday.

CCC 1042-7163/98/070665-04

TABLE 1 Rate Constants and Activation Parameters of the Reaction



$$R_3\overset{\oplus}{P}CH_2\underset{COOR'}{\overset{\ominus}{C}}{-}CN + Ar{-}NCO \xrightarrow{k_{II}} R_3\overset{\oplus}{P}CH_2\overset{\ominus}{C}(C(=O)N(Ar)COOR'){-}CN$$

R = i-Pr

(acetonitrile, 30°C)

Ar	*λ, nm*	k_{II}, *1/mol·min*$^{-1}$	*ΔH*$^{\neq}$*, kcal/mol*	−*ΔS*$^{\neq}$*, e.u.*	*σ**
C_6H_5	300	0.030	9.58	41.5	0.64
α-Naphthtyl	330	0.034	9.15	42.2	0.70
p-$MeOC_6H_4$	305	0.095	8.58	43.1	0.74
3,4-$Cl_2C_6H_4$	305	0.488	7.15	44.54	1.10
o-$O_2NC_6H_4$	370	37.73	2.66	50.72	1.88

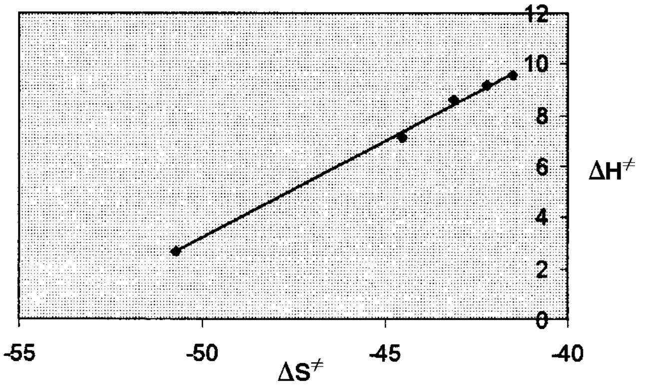


FIGURE 1 Isokinetic relationship in reaction of phosphabetaine **I** with substituted aryl isocyanates (acetonitrile, 30°C).

The kinetic results obtained—in particular, the highly negative values of the activation entropy—indicate, in general, a reaction combining two molecules to form a very polar adduct, but also a highly regular structure of the transition state that is distinctive for cyclic structures. In general, the results are consistent with the previously suggested mechanism [1]. Most probably, a nucleophilic attack of the phosphabetaine anionic center on the carbonyl carbon atom of the isocyanate group and nucleophilic attack of the nitrogen atom on the carbonyl carbon atom of the carbethoxy group, leading to a rupture of C–C bond, are occurring relatively synchronously within the framework of a single transition state (Scheme 1).

The driving force of the reaction is probably influenced by steric hindrance within the activated complex and also by an energetic gain from the more effective delocalization of anionic charge in the product being formed.

Such a mechanism is also supported by the observed influence of substituents in the aryl isocyanate aromatic ring on the reaction rate. When going from the nonsubstituted phenyl isocyanate to the *ortho*-nitro derivative, the reaction rate is increased about 1000-fold (Table 1), which is in a good agreement with the concept of nucleophilic attack of the phosphabetaine on the carbonyl carbon atom of the isocyanate group being the rate-limiting step of the reaction. Also there is a good correlation between $\lg k_{II}$ and Taft's σ^*-constants of the aromatic substituents (Equation 2, Figure 2):

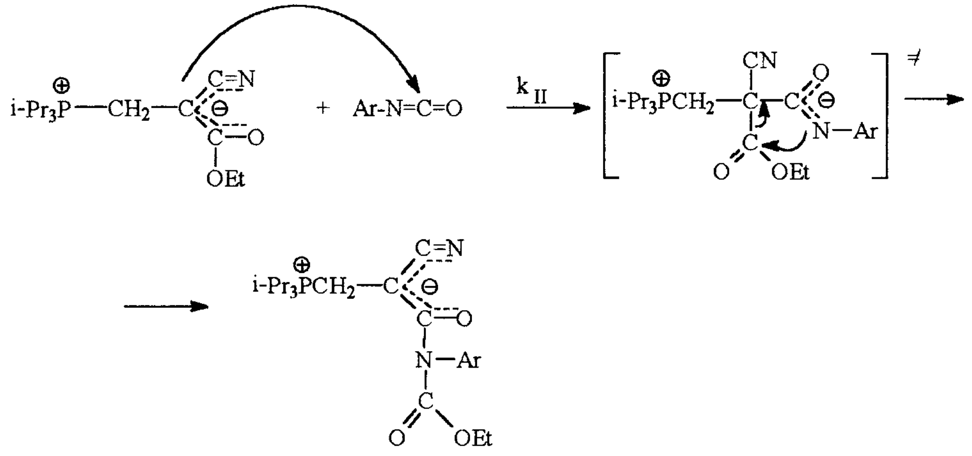
$$\lg k_{II} = -(3.049 \pm 0.510) + (2.469 \pm 0.450)\,\sigma^* \quad (2)$$

$$N = 5,\ R = 0.9950,\ S_o = 0.022$$

A large enough positive value of the parameter ρ (+2.469) in this correlation indicates a high polarity of the transition state, which is in a good agreement with the mechanism suggested.

The next stage of the kinetic investigation was the study of the influence of solvents on the reaction rate. For this purpose, the relatively rapid reaction of the phosphabetaine **I** with the *ortho*-nitrophenyl isocyanate has been chosen. The results obtained are presented in Table 2.

Treatment of the data obtained in accordance with the Koppel-Palm equation shows a significant contribution of three solvent parameters out of four possible ones, namely: polarity Y and polarizability P, reflecting nonspecific interactions, and electrophilicity E, which reflects the general acidic properties of the solvent and its ability to solvate nucleo-



SCHEME 1

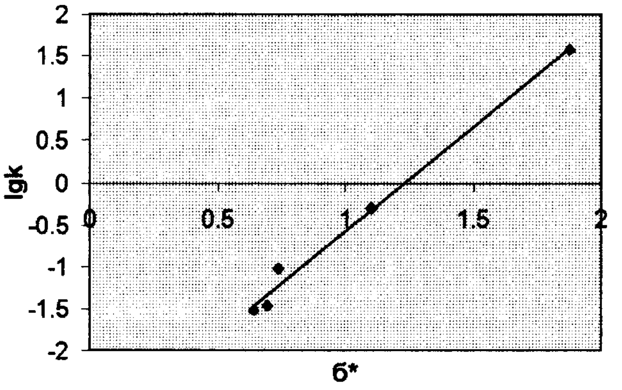


FIGURE 2 Relationship between lgk_{II} and σ^*-constants of aromatic substituents in the aryl isocyanates.

TABLE 2 Solvents Influence in Reaction of Phosphabetaine **I** with *ortho*-Nitropheynl Isocyanate (30°C)

Solvent	k_{II}, *l/mol·min*$^{-1}$	*Y*	*P*	*E*
Dioxane	10.5	0.2231	0.338	4.2
Toluene	13.4	0.2395	0.383	1.3
Ethyl formiate	5.26	0.402	0.298	1.6
Acetone	10.87	0.464	0.297	2.1
Acetonitrile	37.73	0.4803	0.285	5.2

philic centers of the reagents even though there is little influence of these parameters on E.

The three-parameter regression obtained has an excellent quality and reproduces the experimental data with a high degree of accuracy (Equation 3, Figure 3):

$$lgk = -5.278 + 4.120\ Y + 13.487\ P + 0.197\ E \qquad (3)$$

$$N = 5,\ R = 0.9997,\ S_o = 0.00026$$

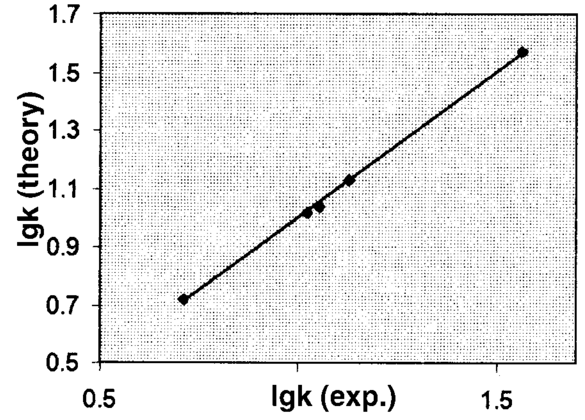


FIGURE 3

The results are also in a good agreement with the mechanism suggested, reflecting a greater polarity and nucleophilicity of the transition state in comparison with the starting reagents.

KINETIC EXPERIMENTS

The kinetics of reaction of the zwitter-ion 1(R = i-Pr, R′ = Et) [1] with each aryl isocyanate was studied by the spectroscopic method on spectrophotometers SP-26 in the temperature interval 20–60°C. The reactions with phenyl isocyanate and 3,4-dichlorophenyl isocyanate were carried out under pseudo–first-order conditions by use of the wavelength 300–330 nm of the zwitter-ion in a high concentration excess of isocyanate, varied from 0.1 to 0.3 M. In the case of *o*-nitrophenyl isocyanate, which is characterized by a strong absorption in the indicated field, an inverse relationship of reagents was used. The isocyanate was taken as the limiting reagent, and the kinetic study was conducted by following the change of the absorption at wavelength 370 nm. In all cases, a reproducible increase of optical density was observed. It is indicated that the reaction products have more strongly chromophoric properties at that wavelength than the starting reagents.

The rate constants of pseudo first order were calculated by the method of minimum quadrants of the tangent of the angle of incline of the kinetic curve anamorphosis in $\ln(D_{max-}\ D_x) - t$ coordinates, where D_x is the actual value of optical density, D_{max}, the max optical density at the end of the reaction, and t, time. In the kinetic experiment, the value of the transmission factor, connected with optical density by the relation $D = -\lg(T/100)$, was measured by help of a digital voltmeter.

The constants of second-order rates were found by dividing k_1 by the concentration of the excess component of the reaction mixture.

REFERENCE

[1] Yu. G. Gololobov, N. A. Kardanov, V. N. Khroustalyov, P. V. Petrovskii, *Tetrahedron Lett, 38,* 1997, 7437.