REACTION OF 1,3-DIPHENYLTRIAZENE WITH PHENYL ISOCYANATE. SOLVENT EFFECT, ACTIVATION PARAMETERS AND KINETIC ISOTOPIC EFFECT

Erhard LEJDAR, Oldřich PYTELA, Miroslav VEČEŘA and Pavel VETEŠNÍK

Organic Chemistry Department,
Institute of Chemical Technology, 532 10 Pardubice

Received July 16th, 1960

Effect of 14 solvents has been studied on the reaction of phenyl isocyanate with 1,3-diphenyltriazene. For ten of these solvents temperature dependence of the reaction velocity has been determined and the respective activation parameters calculated. Hydrogen atom of the triazene imino group has been replaced by deuterium, and the deuterium kinetic isotopic effect has been studied in seven solvents. The results confirm the mechanism suggested in a previous communication.

In a communication of this series[1] a mechanism of the reaction studied was suggested consisting in approach of the phenyl isocyanate molecule above the plane of 1,3-diphenyltriazene and subsequent electron transfer from the p_z orbital of the nitrogen 1 (HOMO) to the p_z orbital of the carbonyl carbon (LUMO). Thereby formation of intramolecular hydrogen bond is facilitated, and planar six-membered ring of the reaction intermediate is formed. From the latter the product (N-phenylazo-N,N'-diphenylurea) is formed by mere electron shift inside the ring.

Such type of reactions can exhibit an "inverse" primary deuterium kinetic effect[2]. According to some papers[3-5] the inverse isotopic effects are due to increase of vibration frequencies of solvent molecules accompanying formation of transition states. Hence the energy involved is that needed for destruction of the solvated reactant particles. Theoretically[5-8] the inverse deuterium isotopic effect can be encountered in the cases where the transition state is "similar to reactants", *i.e.* its formation is not accompanied by substantial structural changes. Another cause of the secondary inverse deuterium kinetic effects is the changed basicity of the reactant particles due to higher electropositivity of deuterium[4]. Hybridization change also plays an important part[6]. The kinetic isotopic effect of the system studied has not yet been investigated.

Temperature effects were studied first of all in the reactions of isocyanates with alcohols. Dyer and coworkers[9] found the activation energy of the reaction of phenyl isocyanate with 1- and 2-butanol to be 33·8 and 41·4 kJ mol^{-1}, respectively. Lovering and Laidler[10] found the following activation parameters of the reactions of phenyl isocyanate with 1-butanol, 2-butanol, and 2-methyl-1-propanol: $\Delta H^{\ddagger} = 48{\cdot}1$, $52{\cdot}3$, and $48{\cdot}1$ kJ mol^{-1}, respectively; $\Delta S^{\ddagger} = -154{\cdot}4$, $-150{\cdot}2$, and $-154{\cdot}4$ J mol^{-1} K^{-1}, respectively. From the large negative activation entropy change the authors infer charge separation in the activated complex. For the reaction of 3-chlorophenyl isocyanate with methanol in heptane the found[11] values of activation energy and activation entropy change were $34{\cdot}3$ kJ mol^{-1} and $-186{\cdot}2$ J mol^{-1} K^{-1}, respectively. The reaction was accelerated by catalyst due to its lowering the activation enthalpy and absolute value of activation entropy. If the reacting alcohol acted as the catalyst, then the activation energy and entropy changed to $28{\cdot}0$ kJ mol^{-1} and $-99{\cdot}2$ J . . mol^{-1} K^{-1} (ref.[12]). For the reaction of phenyl isocyanate with 1-butanol in toluene catalyzed with tributylamine the found[13] activation parameters were $\Delta H^{\ddagger} = 13$ kJ . . mol^{-1} and $\Delta S^{\ddagger} = -254$ J mol^{-1} K^{-1}. Japanese authors[14] studied temperature effect on reaction of isocyanates with amines and found more negative activation entropy and smaller activation enthalpy as compared with the reaction of the same isocyanates with hydroxyl ions in water. In all the cases given the large negative activation entropy change indicates a high degree of organization of the reactants in the transition state.

TABLE I

Reaction Rate Constants of 1,3-Diphenyltriazene with Phenyl Isocyanate in Various Solvents at 25°C

No	Solvent	$k_{obs} . 10^3$ [a] s^{-1}	R[b] %	c_F[c] $. 10^2$ mol l^{-1}	$k_1 . 10^3$ l mol^{-1} s^{-1}	$\frac{\varepsilon - 1}{2\varepsilon + 1}$[d]
1	Pentane	6·0935	1·53	5·438	112·047	0·180
2	Hexane	7·2984	1·92	7·648	95·426	0·186
3	Heptane	5·7288	1·48	5·795	98·855	0·191
4	Isooctane	5·8658	2·83	6·030	97·275	0·197
5	Cyclohexane	6·0823	0·94	7·648	79·526	0·203
6	Benzene	5·0476	1·49	7·648	65·997	0·231
7	Dioxane	0·7516	1·51	6·181	12·218	0·231
8	Diethyl ether	0·8489	0·55	7·599	11·171	0·345
9	Ethyl acetate	0·8232	2·24	7·599	10·833	0·385
10	Tetrahydrofuran	0·7483	1·74	7·648	9·784	0·407
11	3-Methyl-2-butanone	1·3500	1·59	6·587	20·495	0·442
12	4-Methyl-2-pentanone	0·9261	1·80	5·438	17·030	0·449
13	2-Butanone	2·2191	1·35	6·587	33·689	0·461
14	Acetone	1·6845	2·10	5·438	30·977	0·466

[a] 1,3-Diphenyltriazene concentration 1·087—1·356 . 10^{-4} mol l^{-1}; [b] mean relative error of determination of k_{obs}; [c] phenyl isocyanate concentration; [d] ε = relative permittivity[16].

EXPERIMENTAL AND RESULTS

Preparation of 1,3-Diphenyl-3-^2H-triazene

1,3-Diphenyltriazene (1·0 g) and 10 ml [O-^{2}H]2-propanol (96% isotopic purity) were mixed in a sealed glass ampoule, heated at 50°C, 5 h, and kept at —5°C 48 h. The separated crystalline solid was collected by suction, washed three times with 1 ml ether, and kept in vacuum over phosphorus pentoxide. Comparison of N^{1}H and N^{2}H vibrational band intensities in the IR spectra showed that the product contains 87% N^{2}H groups.

The solvents used were dried by a long-term standing with suitable drying agents and were purified by distillation. Purification of phenyl isocyanate was described elsewhere[1].

The kinetic measurements were carried out by the technique described in ref.[1]. The solvent effects were followed at various phenyl isocyanate concentrations, the reactants being dissolved and then mixed in the ratio 1 : 1. Each experiment was repeated three times, from the results we obtained the average k_{obs} value and relative error of the measurements; therefrom the bimolecular rate constant value k_1 was calculated (Table I). The activation parameters (Table II) were determined from the rate constants obtained in similar way at 15, 20, 25, 30 and 35°C. The temperature was measured in the cell. For determination of the kinetic isotopic effect one sample of phenyl isocyanate solution in the respective solvent was treated with the deuterated compound, and another sample was treated with the non-deuterated one. Each experiment was carried out three times. In these cases only the pseudomonomolecular constants k_{obs} were evaluated and used for calculation of the value of isotopic effect (Table III). All the calculations were carried out on an ADT 4100 computer by the described[15] methods using our programs.

TABLE II

Activation Parameters of Reaction of 1,3-Diphenyltriazene with Phenyl Isocyanate in Various Solvents

Solvent	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	Correlation coefficient[a]
Cyclohexane	37·00 ± 1·2	160·8 ± 4·1	0·9932
Heptane	41·8 ± 1·6	146·0 ± 5·3	0·9948
Isooctane	46·5 ± 2·4	128·9 ± 8·1	0·9963
Benzene	52·8 ± 2·2	114·4 ± 7·3	0·9952
Acetone	62·6 ± 4·9	97·9 ± 6·3	0·9858
4-Methyl-2-pentanone	59·2 ± 1·3	92·7 ± 4·5	0·9924
Tetrahydrofuran	65·6 ± 2·1	85·9 ± 6·8	0·9982
Dioxane	65·3 ± 1·6	54·7 ± 5·4	0·9952
2-Butanone	67·3 ± 2·3	50·7 ± 7·6	0·9924
Ethyl acetate	67·2 ± 3·0	47·8 ± 9·9	0·9868

[a] The activation parameters were calculated by regression of linear form of the Eyring equation.

DISCUSSION

The reaction of phenyl isocyanate with 1,3-diphenyltriazene represents a reaction between two dipolar particles. Therefore, according to the Laidler–Eyring equation[17] the plot of logarithm of the bimolecular rate constants against the value[16] $(\varepsilon - 1) : (2\varepsilon + 1)$ should be linear. As the Table I and Fig. 1 show this presumption is fulfilled only partially. Linear dependences only exist within series of cognate solvents. A good linear dependence is found with hydrocarbons (points *1* to *6*) and with tetrahydrofuran and ethyl acetate (points *9* and *10*). The latter two solvents together with dioxane and diethyl ether (points *7* and *8*) shown also another linear dependences. The points corresponding to the remaining four solvents (ketones *11–14*) and those of tetrahydrofuran and ethyl acetate can be interlaced only very roughly with a third straight line. The fact that these three straight lines intersect practically in one point corresponding to tetrahydrofuran (point *10*) is obviously accidental. The only conclusion which can be derived therefrom is that tetrahydrofuran (in the reaction studied) represents a solvent connecting the properties of all the media used. Very different slopes of the straight lines indicate solvation effects to be important in the system besides electrostatic interactions. Large reaction rate in hydrocarbon solvents and linear dependence on the electrostatic term of the Laidler–Eyring equation suggest that in this case the main effect is that of polarity, and the solvent does not solvate the reactants and the activated complex. On the contrary position of the points *7* to *10* and the fact that the reaction rate is lowered by orders of magnitude in oxygen-containing solvents (ethers, esters) indicate a significant influence of non-electrostatic interactions and almost complete independence of the reaction rate on relative permittvity of medium. Retardation of the reaction indicates solvation of reactants and necessity of overcoming of enhanced energy barrier on formation

TABLE III

Kinetic Deuterium Isotope Effect in Reaction of 1,3-Diphenyltriazene with Phenyl Isocyanate

Solvent	$k^{H}_{obs} . 10^3 s^{-1}$	$k^{D}_{obs} . 10^3 s^{-1}$	k^H/k^D
Heptane	11·451	11·303	1·01
Cyclohexane	11·682	11·900	0·98
Benzene	7·904	7·832	1·01
Acetone	0·452	0·529	0·86
Tetrahydrofuran	0·199	0·357	0·56
2-Butanone	0·672	0·722	0·93
Ethyl acetate	0·355	0·573	0·62

of the transition complex. Ketonic solvents (points *11*–*14*) lie between these two extreme cases, both the solvation of reactants (decrease in the reaction rate by about 0·5 order of magnitude) and electrostatic interactions being significant. In this case, however, the reaction rate is increased by increasing polarity in contrast to hydrocarbons.

If the studied solvents are arranged roughly according to their proton-acceptor abilities (basicities), then the activation enthalpy of the studied reaction increases, and absolute value of the activation entropy decreases in accordance with increasing possibility of formation of hydrogen bonds (Table II). In the previous communication[1] we suggested the reaction mechanism consisting of the rate-limiting formation of the addition complex and subsequent intramolecular reorganization of electrons. This mechanism is characterized by a large negative activation entropy due to high coordination of the reacting molecules and organization of the transition complex. If the reaction takes place in solvents of higher basicity, both the polar phenyl isocyanate molecules and 1,3-diphenyltriazene are increasingly solvated, the latter being markedy associated in oxygen-containing solvents[18,19]. Thereby activity coefficients of the reactants are decreased. Formation of the activated complex is accompanied by desolvation of the reactants due to approach of the molecules during formation of the bond. If the synchronous mechanism[1] is presumed, little polar non-solvated complex is formed with high activity coefficient, the reaction is slowed down, and the activation enthalpy increases. Desolvation of reactants on formation of the transition state also increases entropy of the system substrate–solvent. This increase partially compensates the entropy change connected with formation of the organized activated complex. The result is a decrease of absolute value of activation entropy depending on increasing basicity of solvent.

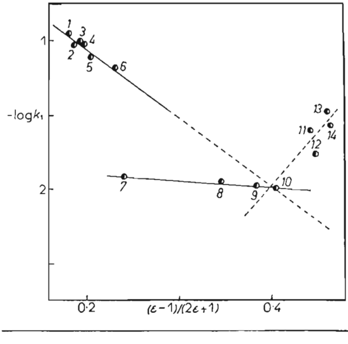

FIG. 1

Dependence of Logarithm of Bimolecular Rate Constant of Reaction of Phenyl Isocyanate with 1,3-Diphenyltriazene on Relative Permittivity of the Solvents Used[16] according to the Laidler–Eyring Equation (for numbers see Table I)

From Table III it is seen that $k^H/k^D \leqq 1$. This result proves unambiguously that the rate-limiting reaction step does not involve a proton-transfer. The ratio k^H/k^D is affected distinctly by solvent; the inverse character is marked in solvating media, it is, however, not proportional to polarity, being lowest in relatively little polar tetrahydrofuran and ethyl acetate.

The inverse character of the deuterium isotopic effect in the reaction of 1,3-diphenyltriazene is obviously due to two effects. *i*) Inductive action of ^2H is more electropositive than that of ^1H (ref.[4]). This fact causes an increase in basicity of the $N_{(1)}$ atom of the triazene chain and better possibility of formation of hydrogen bond. Both these effects facilitate formation of the six-membered cyclic intermediate. *ii*) At both the $N_{(1)}$ atom of 1,3-diphenyltriazene and nitrogen atom of phenyl isocyanate the hybridization is changed from sp^2 to sp^3, which is facilitated by the presence of the more electropositive deuterium atom at $N_{(3)}$ (ref.[4]). The inverse character of the deuterium isotopic effect is made more distinct in oxygen-containing solvents, which is obviously due to solvation of 1,3-diphenyltriazene through formation of hydrogen bond. Its formation makes the both above-mentioned effects more distinct, and the difference of the reaction rates of the ^1H and ^2H compounds increases, which results in a decrease of the k^H/k^D value.

In conclusion it can be stated that the given experimental results agree with the findings published earlier and confirm the suggested reaction mechanism of 1,3-diphenyltriazene with phenyl isocyanate which is entirely different from the known mechanisms of reactions of this compound with other nucleophiles.

REFERENCES

1. Plandorová B., Pytela O., Večeřa M., Vetešník P.: This Journal *45*, 1279 (1980).
2. Collins C. J., Bowman N. S.: *Isotope Effects in Chemical Reactions*, p. 9. Van Nostrand Reinhold, New York 1970.
3. Westheimer F. H.: Chem. Rev. *61*, 265 (1961).
4. Laszlo P., Welvart T.: Bull. Soc. Chim. Fr. *1966*, 2413.
5. Johnston H. S.: *Gas Phase Reaction Rate Theory*, p. 98. Ronald Press, New York 1966.
6. Mitton C. G., Fresser M., Schowen R. L.: J. Amer. Chem. Soc. *91*, 2045 (1969).
7. More O'Ferrall R. A.: Chem. Commun. *1969*, 114.
8. Alder R. W., Baker R., Brown J. M.: *Mechanism in Organic Chemistry*, p. 19. Wiley-Interscience, London 1971.
9. Dyer E., Taylor H. A., Mason S. J., Samson J.: J. Amer. Chem. Soc. *71*, 4106 (1949).
10. Lovering E. G., Laidler K. J.: J. Chem. *40*, 26, 31 (1962).
11. Nesterov O. V., Entelis S. G.: Kinet. Katal. *6*, 178 (1965)
12. Entelis S. G., Nesterov O. V., Zabrodin V. B.: Kinet. Katal. *7*, 627 (1966).
13. Burkus J., Eckert C. F.: J. Amer. Chem. Soc. *80*, 5948 (1958).
14. Higuchi M., Takeshita K., Senju R.: Bull. Chem. Soc. Jap. *47*, 1451 (1974).
15. Pytela O., Večeřa M., Vetešník P.: Chem. Listy *73*, 754 (1979).
16. Landolt-Börnstein: *Zahlwerte und Funktionen*, Vol. 6, p. 618. Springer, Berlin 1959.

17. Amis E. S.: *Solvent Effects on Reaction Rates and Mechanisms*, p. 59. Academic Press, New York 1966.
18. Lazniewski M., Mokrzan J.: Z. Phys. Chem. (Leipzig) *235*, 260 (1967).
19. Hunter L.: J. Chem. Soc. *1937*, 320.

Translated by J. Panchartek.