

REACTIONS OF SUBSTITUTED 1,3-DIPHENYLTRIAZENES WITH PHENYL ISOCYANATES. CATALYSIS AND SUBSTITUENT EFFECTS

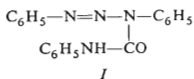
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Reactions of phenyl isocyanate with 12 monosubstituted and 15 symmetrical disubstituted 1,3-diphenyltriazenes have been studied in tetrahydrofuran at 25°C. The found rate constants correlate with the Hammett substituent constants, the slopes being -1.206 and -1.682 in case of the monosubstituted and the disubstituted compounds, respectively. Under conditions of pseudo-monomolecular reaction catalysis by the products and that by the catalysts used in reactions of isocyanates with amines or hydroxy compounds have not been observed. Rates of reactions of 6 substituted phenyl isocyanates with the parent 1,3-diphenyltriazene have also been measured. In this case the found rate constants correlate with the Hammett substituent constants, the slope being $+1.038$. The results indicate that the reaction involves rate limiting formation of a six-membered cyclic complex which successively undergoes only a rapid reorganization of electrons.

Reactions of 1,3-diphenyltriazenes with phenyl isocyanates give N-carbamoyltriazenes (N-phenylazo-N,N'-diphenylureas) *I*.

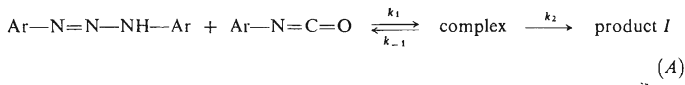


Some members of this compound group are biologically active especially as selective herbicides^{1,2}. A number of papers deal with reactions of isocyanates and amines, alcohols or phenols²⁻⁵, however, the reaction with triazenes has not yet been studied kinetically. In studies of reactions of substituted anilines with phenyl isocyanate it was observed that reactivity of the amino group depends linearly on electron density at nitrogen and fulfils the basic Hammett relation³. Electron-acceptor character of phenylazo group in 1,3-diphenyltriazene causes (as compared with aniline molecule) lowering of the electron density at nitrogen of NH group, *i.e.* lowering of nucleophilicity and increased trend for splitting off of the proton. The reactions of isocyanates with nucleophiles show a general feature – catalysis by products – which was observed in their reactions with both amines⁴ and alcohols^{5,6}. It is presumed^{7,8} that the reaction involves formation of a complex which is then con-

verted irreversibly to products. Rates of establishing of the equilibrium are much higher than those of decomposition of the complexes, and the rate limiting step consists in a proton transfer in the intermediate (the deuterium isotopic effect $k_H/k_D = 1.3$ to 2.0)⁹.

Results of studies of general base catalysis showed that catalytic effect is the greater the higher is basicity of the catalyst. The catalytic activity increases in the series: urea ($K_B \approx 10^{-11}$) < pyridine ($K_B = 2.3 \cdot 10^{-9}$) < triethylamine ($K_B = 5.5 \cdot 10^{-4}$) (ref.¹⁰). Bifunctional mechanism of catalysis was suggested⁹ for explanation of action of ureas the activity of which is increased by electron-donor substituents. Similar results were also obtained in reactions of isocyanates with alcohols¹¹. It was found, that the first step consists in formation of a primary adduct between isocyanate and alcohol, the second one involves splitting off of the proton from this adduct by action of a base, and in the third one the proton is transferred to nitrogen atom of urethane anion. The reactions with alcohols are effectively catalyzed by metal compounds (naphthenates, caprylates or dibutyltin dilaurate¹²).

On basis of available knowledge about reactions of isocyanates with nucleophiles the non-catalyzed reaction of phenylisocyanate with 1,3-diphenyltriazene can be expressed by Eq. (A) where Ar means aryl or substituted aryl group.



Our purpose was to measure the reaction kinetics of the above reaction component carrying various substituents.

EXPERIMENTAL AND RESULTS

Reagents. The substituted 1,3-diphenyltriazenes used in this work were described in the previous communication¹. Phenyl isocyanate was distilled before each measurement. The stock solutions were not kept longer than 24 h. The substituted phenyl isocyanates were commercial chemicals and were purified in the same way as the parent phenyl isocyanate. The tetrahydrofuran used as the reaction medium was stabilized with hydroquinone and was dried by standing with sodium metal at room temperature for one week and by boiling with sodium for 4 h. The dried solvent was distilled with exclusion of air moisture before each series of measurements (each day).

The kinetic measurements were carried out spectrophotometrically with a Zeiss Specord UV-VIS apparatus, the triazene concentration decrease being followed at the wavelength of the main absorption maximum¹. The triazene solutions for the measurements had the concentrations within 10^{-5} to 10^{-4} mol l⁻¹, and the phenyl isocyanate solutions were added thereto at the concentrations enabling pseudomonomolecular course of the reactions (Tables I–IV). The measurements were carried out in 2 cm cells at $25 \pm 0.1^\circ\text{C}$. The rate constants were calculated from the relation $E = E_\infty - (E_0 - E_\infty) \exp(-kt)$, where E_0 , E_∞ and E stand for absorbance

TABLE I

Dependence of Rate Constants of Reaction of 1,3-Diphenyltriene on Concentration of Phenyl Isocyanate

c^a mol l^{-1}	$k_{\text{obs}} \cdot 10^3$ s^{-1}	$k_1 \cdot 10^3$ $\text{l mol}^{-1} \text{s}^{-1}$
0.01	0.028	2.800
0.05	0.158	3.160
0.08	0.286	3.575
0.10	0.376	3.760
0.20	0.765	3.825
0.40	1.750	4.375
0.50	2.230	4.460
0.60	2.671	4.452
0.80	3.566	4.458
1.00	4.446	4.446

^a Concentration of phenyl isocyanate in the reaction mixture.

TABLE II

Rate Constants of Reaction of Monosubstituted 1,3-Diphenyltriazenes with Phenyl Isocyanate in Tetrahydrofuran at 25°C

Comp. No	Substituent	$C_T \cdot 10^{5 \cdot a}$ mol l^{-1}	$k_{\text{obs}} \cdot 10^3$ s^{-1}	$R, \%^b$	C_F^c mol l^{-1}	$k_1 \cdot 10^3$ $\text{l mol}^{-1} \text{s}^{-1}$
1	3-C ₂ H ₅ O	1.36	6.084	3.05	0.631	6.473
2	4-CH ₃	1.42	9.860	1.93	0.631	15.626
3	3-Cl	1.66	2.104	2.30	0.631	3.334
4	4-Cl	2.01	2.566	3.65	0.539	4.761
5	3-Br	1.32	2.010	1.12	0.631	3.185
6	4-Br	1.40	3.259	3.74	0.635	5.132
7	3-CH ₃ CO	1.56	2.092	1.86	0.631	3.315
8	4-CH ₃ CO	1.27	1.742	2.90	0.631	2.760
9	3-CN	1.12	1.362	2.01	0.631	2.159
10	4-CN	1.17	1.080	2.77	0.613	1.712
11	3-NO ₂	1.35	0.828	1.86	0.631	1.312
12	4-NO ₂	1.42	0.666	2.69	0.631	1.056

^a The triazene concentration; ^b mean relative error in determination of k_{obs} ; ^c phenyl isocyanate concentration.

at $t = 0$, $t > 7$ halfives, and t , respectively. Each experiment was repeated three times. The calculations were carried out by the method suggested previously¹³ to give average values k_{obs} (Tables II–IV).

The minimum necessary concentration of the second component was determined by a series of measurements in which phenyl isocyanate concentration was varied within 0.01 to 1.00 mol l⁻¹. Results of these experiments show (Table I) that 500 fold excess of phenyl isocyanate is sufficient for pseudomonomolecular reaction course.

The Hammett correlations of the rate constants and the substituent constants according to McDaniel and Brown¹⁴ are given in Fig. 1, 2 and 3 for monosubstituted triazenes, disubstituted triazenes and substituted phenyl isocyanates, respectively.

Effect of catalysts was followed in reaction of 1,3-bis-(4-chlorophenyl)triazene under the same conditions as above. The triazene and the minimum phenyl isocyanate concentrations were $1.86 \cdot 10^{-5}$ and 0.5 mol l⁻¹, respectively. Concentration of the catalysts and results of the measurements are given in Table V.

The quantum-chemical calculations were carried out by the MINDO/2 method using standard parametrization^{15,16}. The Cartesian coordinates were calculated from general lengths of the individual bonds^{16,17}, standard angles 120°, and planarity of the molecules. The reacting species were considered to have conformations II and III. The phenyl isocyanate geometry was optimized by the procedure suggested by Payne¹⁸. No marked changes took place in position of the centres and in the charge distribution during the optimization. Total charges at the key atoms

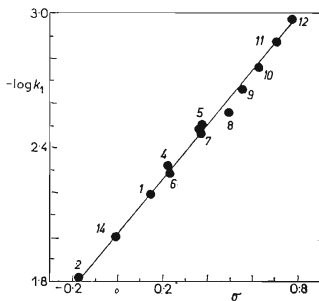


FIG. 1

Correlation of Bimolecular Rate Constants with the Hammett Substituent Constants for Reaction of Monosubstituted 1,3-Diphenyltriazenes with Phenyl Isocyanate

For numbers see Table II.

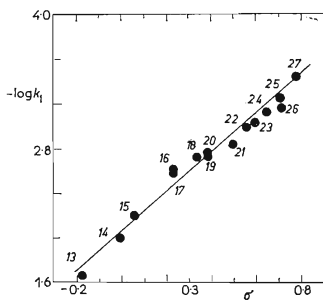


FIG. 2

Correlation of Bimolecular Rate Constants with the Hammett Substituent Constants for Reaction of Symmetrical Disubstituted 1,3-Diphenyltriazenes with Phenyl Isocyanate

For numbers see Table III.

TABLE III

Rate Constants of Reaction of Symmetrical Disubstituted 1,3-Diphenyltriazenes with Phenyl Isoyanate in Tetrahydrofuran at 25°C

Comp. No	Substituent	$C_T \cdot 10^{5,a}$ mol l ⁻¹	$k_{obs} \cdot 10^3$ s ⁻¹	$R, \%^b$	C_F^c mol l ⁻¹	$k_1 \cdot 10^3$ l mol ⁻¹ s ⁻¹
13	4,4'-CH ₃	2.80	11.402	2.80	0.515	22.140
14	H	3.11	5.039	0.89	0.515	9.784
15	4,4'-F	1.59	3.522	5.71	0.563	6.258
16	4,4'-Cl	3.12	1.625	1.80	0.515	3.154
17	4,4'-Br	1.26	1.594	0.22	0.515	3.095
18	3,3'-F	2.34	0.962	0.49	0.515	1.868
19	3,3'-Br	1.08	0.910	0.39	0.515	1.767
20	3,3'-Cl	2.00	0.925	0.38	0.515	1.797
21	4,4'-CH ₃ CO	2.13	0.768	4.15	0.515	1.491
22	3,3'-CN	1.20	0.522	1.96	0.515	1.014
23	3,3'-CH ₃ SO ₂	1.47	0.484	0.43	0.515	0.940
24	4,4'-CN	1.16	0.394	2.14	0.515	0.765
25	3,3'-NO ₂	1.60	0.295	0.83	0.516	0.572
26	4,4'-CH ₃ SO ₂	1.45	0.363	4.02	0.514	0.706
27	4,4'-NO ₂	1.78	0.187	3.26	0.515	0.363

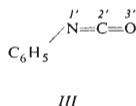
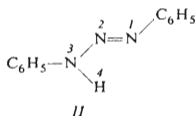
^a The triazene concentration; ^b mean relative error in determination of k_{obs} ; ^c the phenyl isocyanate concentration.

TABLE IV

Rate Constants of Reaction of 1,3-Diphenyltriazene with Substituted Phenyl Isoyanates in Tetrahydrofuran at 25°C

Comp. No	Substituent	$C_T \cdot 10^{5,a}$ mol l ⁻¹	$k_{obs} \cdot 10^3$ s ⁻¹	$R, \%^b$	C_F^c mol l ⁻¹	$k_1 \cdot 10^3$ l mol ⁻¹ s ⁻¹
28	3-CH ₃ O	2.54	7.840	3.00	0.637	12.307
29	4-CH ₃ O	2.19	3.165	1.89	0.592	5.347
30	3-CH ₃	2.50	5.427	3.73	0.615	8.825
31	4-CH ₃	2.32	3.585	1.64	0.518	6.920
32	3-Cl	2.03	13.873	1.41	0.546	25.408
33	4-Cl	2.12	10.286	2.00	0.578	17.795

^a The triazene concentration; ^b mean relative error in determination of k_{obs} ; ^c the substituted phenyl isocyanate concentration.



and localization of electrons in p_z orbitals are summarized in Tables VI and VII for 1,3-diphenyltriazen and phenyl isocyanate, respectively.

TABLE V

Effect of Catalysts on Reaction Rate of Phenyl Isocyanate with 1,3-Diphenyltriazen in Tetrahydrofuran at 25°C

C_{cat}^a mol l^{-1}	$k_{\text{obs}} \cdot 10^3$ s^{-1}	$R, \%$	$k_1 \cdot 10^3$ $\text{l mol}^{-1} \text{s}^{-1}$	$-\log k_1$
N-Phenylcarbamoyl-(4,4'-dichloro)-1,3-diphenyltriazen ^b				
$0.19 \cdot 10^{-5}$	1.715	0.35	3.331	2.477
$0.48 \cdot 10^{-5}$	1.691	0.97	3.384	2.485
$0.96 \cdot 10^{-5}$	1.737	0.58	3.372	2.472
$1.52 \cdot 10^{-5}$	1.774	0.36	3.443	2.463
Triethylamine ^b				
$0.18 \cdot 10^{-6}$	1.806	0.43	3.506	2.455
$0.92 \cdot 10^{-6}$	1.770	0.39	3.438	2.464
$1.84 \cdot 10^{-6}$	1.747	0.28	3.391	2.470
$9.24 \cdot 10^{-6}$	1.927	0.14	3.744	2.427
Pyridine ^b				
$0.19 \cdot 10^{-6}$	1.990	0.89	3.864	2.413
$0.94 \cdot 10^{-6}$	1.848	0.12	3.588	2.445
$1.88 \cdot 10^{-6}$	1.919	0.17	3.727	2.429
$9.44 \cdot 10^{-6}$	2.080	1.16	4.039	2.394
Dibutyltin dilaurate ^b				
$1.25 \cdot 10^{-6}$	1.717	0.56	3.301	2.481
$6.06 \cdot 10^{-4}$	1.809	1.12	3.479	2.458
$6.96 \cdot 10^{-2}$	1.784	3.54	3.431	2.464

The catalyst concentration; ^b the phenyl isocyanate concentration $C_F = 0.520 \text{ mol l}^{-1}$.

DISCUSSION

Reaction of 1,3-diphenyltriene (*II*) with phenyl isocyanate (*III*) can take various courses differing by structure of the formed transition complex and way of proton transfer in the subsequent step leading to product. Energy levels of HOMO and LUMO of the both reacting species (Fig. 4) show a slightly greater probability

TABLE VI

Total Charges at Key Atoms and Electron Localization in p_z Orbitals in 1,3-Diphenyltriene Molecule

Position	1	2	3	4
$q - Z$	-0.30883	0.00110	-0.23728	0.18889
$c^2(p_z)$ (HOMO)	0.11167	0.04391	0.24338	—
$q(p_z) - Z(p_z)$	-0.13626	-0.00981	0.24240	—

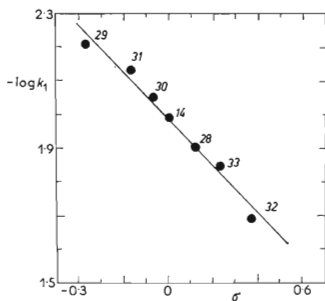


FIG. 3

Correlation of Bimolecular Rate Constants with the Hammett Substituent Constants for Reaction of 1,3-Diphenyltriene with Substituted Phenyl Isocyanates

For numbers see Table IV.

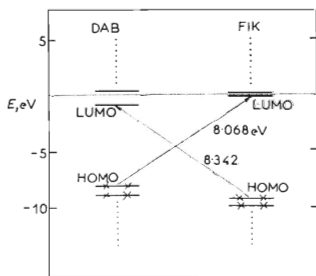


FIG. 4

Energy Levels of Frontier Orbitals of 1,3-Diphenyltriene (DAB) and Phenyl Isocyanate (FIK) Calculated by MINDO/2 Method

of electron transfer from 1,3-diphenyltriazene to phenyl isocyanate. Hence the reaction would be initiated by a nucleophilic attack at carbonyl carbon atom of phenyl isocyanate where its LUMO is localized and where there is the lowest electron density (Table VII). This view is supported experimentally by the value (+1.038) of the q constant of the reaction of substituted phenyl isocyanates with 1,3-diphenyltriazene which shows that the rate limiting step consists in nucleophilic attack at an atom influenced but little by substituents.

The mechanism is less clear from the viewpoint of the nucleophile — 1,3-diphenyltriazene. Its HOMO is localized mainly at nitrogen 3 and nitrogen 1, the electrons being located more in σ and π system at the nitrogen 3 and 1, respectively. The nitrogen atom 2 cannot be considered nucleophilic centre, because the overall electron density is low here, and also HOMO is not localized at this atom (Table VI).

If the nitrogen 3 were the attacking atom, the addition would take place *via* p_z orbitals where HOMO is localized, however, this attack is not probable due to electron deficit here. A charged transition complex would be formed in this case, and a subsequent proton transfer would be necessary either direct from the nitrogen 3 of 1,3-diphenyltriazene to nitrogen of phenyl isocyanate or indirect from the nitrogen 3 to oxygen and then to nitrogen of phenyl isocyanate. In both the cases catalysis would be significant (the proton transfer with the help of a catalyst). However, experimental data show that catalysts have no effect, hence the both mechanisms must be refused (Table V), the proton transfer being obviously not involved in the rate limiting step.

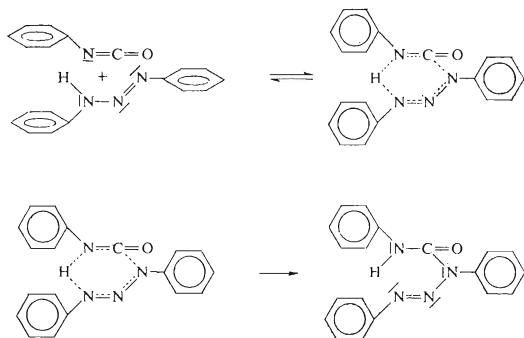
Nucleophilic attack with electron transfer from the nitrogen 1 of the triazene chain can be initiated by approaching of the two partners in the plane of the triazene molecule, *i.e.* by using the free electron pair from sp^2 orbital. Another possibility consists in an approach of the phenyl isocyanate molecule over the plane of 1,3-diphenyltriazene, electrons being transferred from p_z orbital (HOMO) of the nitrogen 1 to p_z orbital (LUMO) of carbonyl carbon atom. In both the cases an energetically favour-

TABLE VII

Total Charges at Key Atoms and Electron Localization in p_z Orbitals of Phenyl Isocyanate Molecule

Position	1'	2'	3'
q	-0.65225	0.92816	-0.53637
$c^2(p_z)$ (HOMO)	0.18120	0.02612	0.05071
$c^2(p_z)$ (LUMO)	0.10802	0.11783	0.03106

able intermediate with six-membered ring would be formed, the proton transfer resulting from mere electron shift. In the latter case the phenyl isocyanate molecule would have to be rotated after the electron transfer from triazene nitrogen to phenyl isocyanate carbon atom, so that the free electron pair at the nitrogen 1' might be available. The latter mechanism seems to be more favourable with respect to less non-bonding interactions as compared to those operating in planar course of linking of the two molecules. Another argument in favour of the latter mechanism is that electrons are transferred from HOMO of 1,3-diphenyltriazene to LUMO of phenyl isocyanate (Scheme 1).



SCHEME 1

The latter mechanism is also supported by experimental results of measurements of substituent effects on the reaction rate. For the monosubstituted 1,3-diphenyltriazenes the Hammett reaction constant was found -1.206 , *i.e.* relatively low and supporting the presumption of formation of the intermediate in which the substituent effect is dispersed to several centres. Similar conclusion can be drawn from the reaction constant obtained for symmetrical disubstituted 1,3-diphenyltriazenes (-1.682). Difference between the both reaction constants is small and indicates again dispersion of the substituent effect.

To sum up it can be stated that from quantum-chemical calculations and experimental results given in this paper the following mechanism (Scheme 1) can be suggested for reaction of phenyl isocyanate with 1,3-diphenyltriazene: The reaction is initiated by electron transfer from the nitrogen 1 of diphenyltriazene to the carbon atom 2' of phenyl isocyanate. The phenyl isocyanate molecule is approaching per-

pendicularly to the plane of the 1,3-diphenyltriazene molecule. Then follows rotation of the phenyl isocyanate molecule by 90° round the N—C—O axis and formation of six-membered ring through partial bonds $N \cdots H \cdots N$. These two steps cannot be differentiated by the methods used and represent the rate limiting equilibrium step. The last rapid step only involves mere reorganization of electrons and formation of final structure of the substituted urea.

Kinetics of the reaction of 1,3-diphenyltriazene with phenyl isocyanate can be described by Eq. (1)

$$d[X]/dt = k_1[T][F] - k_{-1}[X] - k_2[X], \quad (1)$$

where $[T]$, $[F]$ and $[X]$ are concentrations of 1,3-diphenyltriazene, phenyl isocyanate and the transition complex, respectively, and k_i are rate constants of Eq. (A). Steady state treatment gives Eq. (2) for $d[X]/dt = 0$

$$d[P]/dt = -d[T]/dt = (k_1 k_2 / (k_{-1} + k_2)) [T][F] \quad (2)$$

and for the experimentally found condition $k_2 \gg k_1$ and $k_2 \gg k_{-1}$ it follows:

$$-d[T]/dt = k_1[F][T]. \quad (3)$$

If sufficient excess of phenyl isocyanate is present, i.e. $[F] = [F_0] = \text{const.}$, then

$$-d[T]/dt = k_{\text{obs}}[T], \quad (4)$$

where $k_{\text{obs}} = k_1[F_0]$.

REFERENCES

1. Beneš J., Beránek V., Zimprich J., Vetešník P.: This Journal 42, 703 (1977).
2. Bondarenko D. D., Walworth B. L.: U.S. 3 382 061 (1968).
3. Akiyama H., Yoshida N., Araki Y., Onchi K.: J. Chem. Soc. (B), 1968, 676.
4. Baker J. W., Bailey D. N.: J. Chem. Soc. 1957, 4655.
5. Baker J. W., Haldworth J. B.: J. Chem. Soc. 1947, 713.
6. Baker J. W., Gannt.: J. Chem. Soc. 1949, 9.
7. Farkas A., Mills G. A.: Advan. Catal. Relat. Subj. 13, 393 (1962).
8. Baker J. W., Bailey D. N.: J. Chem. Soc. 1957, 4649.
9. Briody J. M., Narineshing D.: Tetrahedron Lett. 44, 4143 (1971).
10. Baker J. W., Bailey D. N.: J. Chem. Soc. 1957, 4663.
11. Herlinger H.: Thesis. Universität, Stuttgart 1969.
12. Sandler S. R., Karo W.: *Organic Functional Group Preparation*, Vol. 12-II, p. 224. Academic Press, New York 1971.
13. Pytela O., Večeřa M., Vetešník P.: Chem. Listy 73, 754 (1979).

14. Chapman N. B., Shorter J.: *Advances in Linear Free Energy Relationships*, p. 28. Plenum Press, London 1972.
15. Dewar M. J. S., Haselbach E.: *J. Amer. Chem. Soc.* **92**, 590 (1970).
16. Bodor N., Dewar M. J. S., Hauget A., Haselbach E.: *J. Amer. Chem. Soc.* **92**, 3854 (1970).
17. Dewar M. J. S., Lo D. H.: *J. Amer. Chem. Soc.* **94**, 5296 (1972).
18. Payne P. W.: *J. Chem. Phys.* **65**, 1920 (1976).

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